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**Natural Attenuation of Chlorinated Solvent Ground-Water  
Plumes Discharging Into Wetlands**

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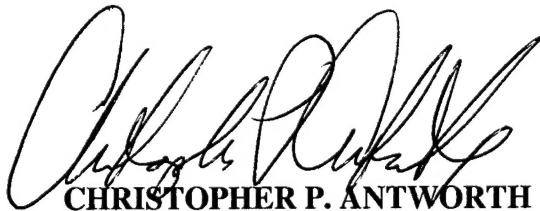
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**NATURAL ATTENUATION OF CHLORINATED SOLVENT  
GROUND-WATER PLUMES DISCHARGING INTO WETLANDS**

**U.S. Geological Survey and Air Force Research Laboratory**

**September 2002**

by Michelle M. Lorah, David R. Burris, Linda Jo Dyer, and Christopher P. Antworth

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## ABSTRACT

A substantial number of chlorinated solvent ground-water plumes at hazardous waste sites are currently discharging, or may potentially discharge, into ecologically sensitive wetland environments. Although chlorinated solvents tend to be relatively resistant to degradation within most aquifer systems, rapid and complete transformations can occur within the organic-rich reducing environment typical of wetland sediments, suggesting that monitored natural attenuation may be an effective remediation option for discharges into wetlands. A previous study by the U.S. Geological Survey (USGS) in a freshwater tidal wetland at Aberdeen Proving Ground (APG), Maryland, showed complete attenuation of chlorinated solvents before the wetland surface or creek was reached. A collaborative study by the USGS and the Air Force Research Laboratory under the Department of Defense Environmental Security Technology Certification Program (ESTCP) was conducted to determine if the natural attenuation of chlorinated solvents that occurs at the APG wetland site can occur at wetland sites located in different hydrogeologic environments and to assist in the transfer of this technology to other potential users. The objectives of this ESTCP demonstration projective were to (1) assess and compare the extent of natural attenuation of chlorinated solvent at three wetland sites in different hydrogeologic environments; (2) to demonstrate and compare different methods of sampling and analysis for collecting the site data needed to evaluate natural attenuation in wetlands; and (3) to develop a technical protocol for the assessment of natural attenuation of chlorinated solvent plumes discharging into wetlands.

The three sites selected for the demonstration were the freshwater wetland at APG, an inland forested bog in the Colliers Mills Wildlife Management Area (WMA) at McGuire Air Force Base, New Jersey, and a spring/seep wetland at Hill Air Force Base, Utah. The APG site was used for comparison to the other wetland sites and to complete the second objective of evaluating different methods of sampling and analysis appropriate for assessing natural attenuation in wetlands. This information was used in the development of a technical protocol for the assessment of natural attenuation of chlorinated solvent plumes discharging into wetlands. Results are presented in 4 sections: (1) introduction to the study and background on the APG site that was used for comparison of the extent of natural attenuation at the other sites, (2) natural attenuation assessment at the Colliers Mills WMA wetland site in New Jersey, (3) results of comparison of sampling and analysis methods for wetland studies that was conducted at the APG site, and (4) protocol addendum for assessing natural attenuation of chlorinated solvents in wetlands.

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# NATURAL ATTENUATION OF CHLORINATED SOLVENT GROUND-WATER PLUMES DISCHARGING INTO WETLANDS

U.S. Geological Survey and Air Force Research Laboratory  
September 2002

## Section 1. Introduction

### 1.1 Background Information

A substantial number of chlorinated solvent ground-water plumes at hazardous waste sites are currently discharging, or may potentially discharge, into ecologically sensitive wetland environments. About 75 percent of Resource Conservation and Recovery Act (RCRA) and Superfund sites, including Department of Defense (DoD) facilities, are located within 0.80 km of a surface-water body (Tomassoni, 2000), where wetlands often are part of the landscape. For example, of the 67 Navy installations that have National Priority List sites, 43 percent are located in coastal areas of California, Florida, Virginia, and Washington (Department of the Navy, 2000). Conventional engineered remediation of ground water contaminated with chlorinated solvents such as trichloroethene (TCE) can be extremely costly and detrimental to wetland ecosystems. Wetland ecosystems support diverse food webs, provide breeding grounds for important commercial species (Boesch et al., 1999), and provide habitat for one third of the species listed as threatened or endangered (U.S. Fish and Wildlife Service, 1990). Potentially damaging, engineered remedial interventions may be avoided if sufficient natural attenuation of the dissolved chlorinated solvents occurs within the wetland sediment zone prior to discharge into the surface water of the wetlands. Although chlorinated solvents tend to be relatively resistant to degradation within most aquifer systems, rapid and complete transformations can occur within the organic-rich reducing environment typical of wetland sediments, suggesting that monitored natural attenuation may be an effective remediation option for discharges into wetlands (Lorah et al., 1997; Lorah and Olsen, 1999a, b; Lorah et al., 2001).

The U.S. Environmental Protection Agency has defined *natural attenuation* as: "naturally-occurring processes in soil and ground-water environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants" (Weidemeier et al., 1996). Because biodegradation is the primary destructive process for many organic ground-water contaminants, it commonly is considered the most critical to demonstrate as effective for natural attenuation to be a feasible remediation alternative. Natural attenuation as a remedial action alternative for contaminants dissolved in ground water has gained considerable acceptance

in recent years, particularly with respect of dissolved petroleum hydrocarbons (for example, Stauffer et al., 1993; Weidemeier et al., 1994; National Research Council, 2000). The use of natural attenuation as a remedial alternative requires an understanding of fate and transport processes, which are contaminant- and site-specific, to assess current or potential threats to human health and the environment.

A number of laboratory and field studies conducted over the past two decades have shown that subsurface microorganisms can biodegrade chlorinated solvents (Wiedemeier et al., 1999), but few studies have assessed the fate of chlorinated solvents in wetlands (Lorah et al., 1997; Lorah and Olsen, 1999b). Wetlands are ideal environments for biodegradation of chlorinated solvents because of the abundance of natural organic substrates, the wide range of redox zones, and the large diversity of microorganisms. The most significant difference between degradation processes for chlorinated solvents compared to fuel hydrocarbons is that biodegradation of chlorinated solvents requires an adequate supply of electron donors (substrates) because the contaminant itself often is not an electron donor for the microorganism (Wiedemeier et al., 1998; National Research Council, 2000). Although many aquifers have a low supply of natural organic matter that can provide electron donors to sustain biodegradation of chlorinated solvents, the abundant natural organic matter in wetland sediments should eliminate electron donor supply as a limiting factor.

During 1992-96, the U.S. Geological Survey (USGS) investigated the natural attenuation of chlorinated solvents in a contaminant plume that discharges from a sand aquifer to a freshwater tidal wetland along the West Branch Canal Creek at Aberdeen Proving Ground (APG), a U.S. Army base in Maryland. This study shows that natural attenuation processes within the 1.8- to 3.6-m-thick wetland sediments greatly reduce chlorinated solvent concentrations and toxicity before the ground water discharges to land surface or the creek (Lorah et al., 1997). Sorption and anaerobic biodegradation, through reductive dechlorination pathways, are two of the primary natural attenuation processes. In microcosms constructed with the wetland sediment, the first-order rate constant for anaerobic degradation of trichloroethylene was about  $0.1$  to  $0.3 \text{ day}^{-1}$ , which is more than 10 times faster than degradation rates reported in the literature for sand aquifers at Picatinny Arsenal, New Jersey, and St. Joseph, Michigan ( $0.0001$  to  $0.003 \text{ day}^{-1}$ ; Rifai et al., 1995). The first-order rate constant for anaerobic degradation of 1,1,2,2-tetrachloroethane (about  $0.2 \text{ day}^{-1}$ ) in the wetland sediments at APG was as high as for TCE. In conjunction with toxicity studies conducted at the site, this investigation has demonstrated that natural attenuation in the wetland could be an effective remediation method for the ground-water contaminant plume (Lorah et al., 1997; Lorah and Olsen, 1999a,b).

This USGS wetland study led to a collaborative study with the Air Force Research Laboratory under the DoD Environmental Security Technology Certification Program (ESTCP). The purpose of the ESTCP study described in this report was to determine if the natural attenuation of chlorinated solvents that occurs at the APG wetland site can occur at wetland sites located in different hydrogeologic environments and to assist in the transfer of this technology to other potential users.

### **1.1.1 Objectives of the Demonstration**

The objectives of this ESTCP demonstration are to (1) assess and compare the extent of natural attenuation of chlorinated solvent at three wetland sites in different hydrogeologic

)

environments; (2) to demonstrate and compare different methods of sampling and analysis for collecting the site data needed to evaluate natural attenuation in wetlands; and (3) to develop a technical protocol for the assessment of natural attenuation of chlorinated solvent plumes discharging into wetlands. The three sites for the demonstration were selected to represent end-members of the wide range of freshwater wetland types that exist (Figure 1.1). Figure 1.1 shows a classification system for wetlands based on dominant water sources. The Colliers Mills Wildlife Management Area (WMA) wetland site near the BOMARC Missile Facility, McGuire Air Force Base (AFB), New Jersey, is an inland forested bog that appears to be a mixture of ground water and precipitation dominated. The West Branch Canal Creek site at APG, Maryland, is a freshwater tidal wetland where surface water is a dominant water source, and the Hill AFB site (OU-4), Utah, is a seep/spring wetland area where ground water is the dominant water source. Although reconnaissance activities at the Colliers Mills WMA wetland site indicated less efficient degradation than at the APG site, it was selected as a demonstration site to gain a better understanding of factors limiting the natural attenuation of chlorinated solvent plumes discharging into wetlands. Several wetland sites examined as potential study sites for this project had detectable concentrations of chlorinated solvents in the surface water, including sites at Robins AFB, Georgia; Shaw AFB, South Carolina; Otis ANGB, Massachusetts; and Cape Canaveral, Florida.

For the APG and Colliers Mills WMA wetland sites, the three recommended lines of evidence to support the occurrence of natural attenuation of chlorinated solvents (Wiedemeier et al., 1996; 1998) were collected: (1) observed reductions in contaminant concentrations along a flowpath downgradient from the contaminant source; (2) geochemical and hydrologic data that demonstrate appropriate redox conditions for biodegradation, provide field evidence of the occurrence of biodegradation, and allow calculation of biodegradation rates at the field scale; and (3) laboratory microbiological data that supports the occurrence of biodegradation and gives potential rates. Although natural attenuation of chlorinated solvents at the West Branch Canal Creek, APG site was assessed previously and determined to be a viable remedial alternative (Lorah et al. 1997; Lorah and Olsen, 1999a,b; Lorah et al., 2001), additional study was done during this ESTCP demonstration to allow comparison to the other wetland sites for the same period. Because phytoremediation instead of biodegradation appeared to be the dominant natural attenuation process for the Hill AFB site, data collection focused on the first line of evidence above and determination of physical attenuation processes. In addition, the APG site was used to complete the second objective of evaluating different methods of sampling and analysis appropriate for assessing natural attenuation in wetlands. This information was used in development of a technical protocol for the assessment of natural attenuation of chlorinated solvent plumes discharging into wetlands.

Evaluation of natural attenuation as a remedial action includes: a) determination and documentation of operational natural attenuation processes; and b) assessment of the level or extent of natural attenuation taking place, as well as its potential for future occurrence, relative to action levels. A protocol for natural attenuation of chlorinated solvents has been prepared by AFCEE and has recently been published as an USEPA document (Wiedemeier et al., 1996; Wiedemeier et al., 1998). It was recognized in this protocol that "For sites where contaminated ground water discharges to surface water, the philosophy of monitoring is not well developed." The focus of the ESTCP demonstration at the APG site was to address the monitoring (site assessment) requirements for the evaluation of natural attenuation in wetland systems where



ground water contaminated with chlorinated solvents discharges. The protocol presented here for natural attenuation assessment in wetlands was written to be an addendum to the AFCEE protocol for natural attenuation of chlorinated solvents (Wiedemeier et al., 1996).

### **1.1.2 Regulatory Issues**

Regulatory acceptance and requirements for monitored natural attenuation as a remedial action currently is evolving and varies between states and USEPA regions. Some regulatory agencies require an estimate of the time required for natural attenuation to completely remove the plume, which can be a difficult task, especially if dense nonaqueous phase liquids (DNAPLs) are present. Natural attenuation in wetlands occurs at the terminus of the plume, and detailed site information within the wetland is required to estimate natural attenuation rates at this terminus. The amount of time required to completely remove the plume by natural attenuation in the wetland, however, is dependent largely on the amount of time required for the plume to be discharged into the wetland, including time needed for flushing and dissolution of DNAPLs in the aquifer upgradient of the wetland and for mass transfer of any contaminants sorbed to clayey layers throughout the aquifer. Additional site information concerning the contaminant source area, therefore, would be required. The acceptance of monitored natural attenuation as a remedial action often may be coupled with an engineered remediation technology to, at least partially, address the contaminant source area. Since source area remediation technologies for DNAPLs generally are only partially effective, it can be advantageous to use monitored natural attenuation as a contaminant removal polishing step. Recent USEPA guidance on the use of monitored natural attenuation states that USEPA expects that source control will be a fundamental component of any monitored natural attenuation remedy (USEPA, 1999).

Regulatory agencies may require a full risk assessment, even though the plume appears to be effectively attenuated within the wetland sediment. Natural attenuation processes in a wetland ground-water discharge situation occur in close proximity to surface water. Because surface water is generally viewed as the exposure pathway completion endpoint, regulatory agencies may be extremely cautious, increasing the need for detailed evaluation of natural attenuation processes. Results of the assessment of natural attenuation can be used for the exposure portion of a risk assessment. As with all efforts to establish remediation plans, the appropriate federal, state and local regulatory agencies need to be involved throughout the process.

### **1.1.3 Advantages and Limitations of the Technology**

Natural attenuation of chlorinated solvents in ground water can be a cost-effective remedial option if the operational natural attenuation processes are able to meet the applicable regulatory criteria. Many available engineered technologies, particular DNAPL source cleanup technologies, may only be partially effective. Thus, even if an alternative engineered remediation technology is selected, it is often necessary to address the lower level of contamination that remains. Natural attenuation can be a cost-effective secondary technology to address any remaining contamination in those cases. Some of the traditional technologies, such as pump-and-treat, can be detrimental to wetland systems by severely reducing the ground-water inflow to the wetland. Ecologically-sensitive wetland systems require water. Avoiding alteration of the wetland's water balance may be the most important criterion in the remedy

selection. Other engineered remedial options that require construction, such as installation of a barrier wall, or sediment removal could impact a wetland's ecosystem by the noise, habitat destruction, or increased sedimentation in the surface water. If the specific wetland has the ability to naturally attenuate the contamination to prevent receptor pathway completion, utilization of that natural ability in a remediation plan could have the least impact on the wetland ecosystem and be most cost-effective.

A disadvantage of utilizing chlorinated solvent natural attenuation in a wetland system is that not all wetlands may contain suitable environments for promoting and sustaining adequate transformation or loss of the contaminants. The wetland system, itself, may be viewed as a receptor. Even if the wetland's subsurface sediment system is not viewed as a receptor, it is very close to the wetland's surface water, which most likely would be viewed as a receptor. Due to the close proximity to a receptor, a more conservative approach may be required in the remedial action selection process, necessitating alternative engineered remedial actions in addition to natural attenuation.



## 1.2 Description of Natural Attenuation Processes in Wetlands

### 1.2.1 Biodegradation

Anaerobic conditions generally exist in wetlands because oxygen diffusion is limited in waterlogged soils and because the high availability of natural organic substrates for microbial respiration causes rapid depletion of oxygen (Mitsch and Gosselink, 2000). The amount of natural organic matter and oxygen typically varies over small depth intervals in wetland sediments, producing steep chemical concentration gradients with varying redox conditions and providing habitat for a large diversity and number of microorganisms. Biodegradation pathways and rates in wetland sediments, therefore, can vary over small vertical scales in ground-water discharge wetlands (Pardue et al., 1993; Lorah and Olsen, 1999b). Biodegradation of highly chlorinated solvents such as TCE occurs under a range of anaerobic conditions (nitrate-reducing, iron-reducing, sulfate-reducing, methanogenic) but is believed to be fastest and most complete under methanogenic conditions (McCarty and Semprini, 1994). In freshwater anaerobic sediments where sulfate concentrations are relatively low, 70 to 92 percent of organic carbon decomposition can be through methanogenesis (Capone and Kiene, 1988). Freshwater wetland sediments, therefore, could provide an ideal environment for natural attenuation of chlorinated solvents.

Organic contaminants can be biodegraded by serving as either an electron donor that becomes oxidized or as an electron acceptor that becomes reduced. Because highly chlorinated volatile organic compounds (VOC's) such as tetrachloroethene (PCE) and TCE have a relatively high oxidation state, they are biodegraded most easily through reduction reactions (rather than through oxidation reactions) under anaerobic conditions. Reductive dechlorination is the most important anaerobic biodegradation process for the highly chlorinated ethenes (PCE, TCE) (Vogel and McCarty, 1985; Freedman and Gossett, 1989; Bouwer, 1994) and proceeds primarily via sequential hydrogenolysis. Thus, PCE degrades sequentially to TCE, dichloroethene (DCE), vinyl chloride (VC), and ethene. For chlorinated ethanes, dichloroelimination also is an important anaerobic dechlorination reaction, resulting in production of an alkene. For example, 1,1,2,2-tetrachloroethane is degraded to 1,2-DCE and 1,1,2-trichloroethane is degraded to VC by dichloroelimination (Jafvert and Wolfe, 1987; Vogel et al., 1987; Lorah et al., 1999a).

Microorganisms do not always gain energy from degradation of contaminants; instead, degradation may be an incidental reaction, commonly referred to as "secondary utilization" or "cometabolism", where the presence of primary substrates to support microbial metabolism is required (National Research Council, 1993). Cometabolic reductive dechlorination can occur through reactive transition metal cofactors, such as vitamin B<sub>12</sub>, heme, and coenzyme F<sub>430</sub>, that catalyze the replacement of chlorines by hydrogen atoms (Fathepure and Boyd, 1988; Gantzer and Wackett, 1991; Schanke and Wackett, 1992; Yager et al., 1997; Novak et al., 1998). These reactive coenzymes are especially abundant in methanogens (anaerobic microorganisms that produce methane predominantly through metabolism of hydrogen plus carbon dioxide or metabolism of acetate) and acetogens (anaerobic microorganisms that synthesize acetate from carbon dioxide through the acetyl-CoA pathway) (Fathepure and Boyd, 1988; Maymó-Gatell et al., 1997; Yager et al., 1997).

In addition to cometabolic anaerobic reactions, pure cultures of anaerobic dehalorespiring bacteria have been isolated that can use chlorinated ethenes, including PCE, TCE, and DCE, as terminal electron acceptors to derive energy and grow (Holliger et al., 1993; Krumholz et al., 1996; Maymó-Gatell et al., 1997, 1999, 2001). This growth-coupled metabolism of chlorinated VOCs generally is believed to be faster than cometabolic reductive dechlorination and, thus, may be more effective for remediation of contaminated ground water (Maymó-Gatell et al., 1997; Yager et al., 1997). Pure cultures of dehalorespiring bacteria that can use PCE and TCE as terminal electron acceptors include *Dehalospirillum multivorans*, *Dehalobacter restrictus* strains PER-K23A and TEA, *Desulfuromonas* sp. strain BB1 and *Desulfuromonas chloroethenica*, *Enterobacter* sp. strain MS1, *Desulfitobacterium* sp. strain PCE-S, and *Dehalococcoides ethenogenes* strain 195 (Löffler et al., 2000). *Dehalococcoides ethenogenes* is the only known isolate that completely dechlorinates PCE or TCE to ethene (Maymó-Gatell et al., 1997). The only chlorinated ethane reported to be degraded by dehalorespiring bacteria is 1,2-dichloroethane (Maymó-Gatell et al., 1997, 1999).

Wetlands are one of the few soil and ground-water environments where both anaerobic and aerobic degradation of chlorinated VOC's could occur. Aerobic conditions are usually present in a thin surficial layer of wetland sediments, and many wetland plants transport oxygen from the atmosphere to their roots (Mitsch and Gosselink, 2000). Lower chlorinated VOCs, such as DCE and VC, can be biodegraded aerobically through cometabolic reactions and through growth-coupled mineralization reactions. Methanotrophs, bacteria that utilize methane as their primary substrate, have been associated with cometabolic biodegradation of chlorinated solvents under aerobic conditions. Methanotrophs are generally most active at the interface between aerobic and anaerobic zones, including along roots in wetland sediments (King, 1994). With chlorinated alkenes such as TCE, methanotrophic degradation forms epoxides that are chemically unstable and can be transformed rapidly by abiotic hydrolysis to nonvolatile products, including aldehydes and acids. Heterotrophic microorganisms can further metabolize these products to carbon dioxide, chlorine, and water (Little et al., 1988). Growth-coupled anaerobic oxidation (or mineralization) of VC to carbon dioxide (CO<sub>2</sub>) or to CO<sub>2</sub> and methane (CH<sub>4</sub>) has been reported in laboratory experiments under iron-reducing, sulfate-reducing, humic acid-reducing, and methanogenic conditions (Vogel and McCarty, 1985; Bradley and Chapelle, 1996, 1998, 1999; Bradley et al., 1998). 12DCE also can undergo anaerobic oxidation, but at substantially slower rates than those observed for VC (Bradley et al., 1998).

### 1.2.2 Physical Processes

Physical (or physical-chemical) processes that can be important in wetland sediments include sorption, dispersion, and plant uptake. Volatilization is likely to be insignificant in wetland sediments that are saturated to land surface. Plant uptake (phytoremediation) can include both physical transport through transpiration and degradation or transformation of the contaminant with the plant.

Wetland sediments typically have a high content of natural organic matter that can sorb hydrophobic organic contaminants. Sorption is the partitioning of dissolved solutes from the ground water onto the particles comprising the aquifer matrix. Because of their nonpolar structure, chlorinated VOC's most commonly sorb through hydrophobic forces (Chiou et al.,

1979; Schwarzenbach and Westall, 1981). Although sorption retards movement of the contaminant plume relative to the advective ground-water-flow velocity, sorption is a reversible reaction so contaminants are not permanently removed from solution. Sorption is a complex process that can be caused by several mechanisms, including hydrogen bonding, chemisorption, and hydrophobic forces. Distribution coefficients ( $K_d$ 's) that describe the partitioning of hydrophobic contaminants between sorbed and dissolved phases have been found to correlate well with the fraction of organic carbon in the soil or sediment if the fraction of organic carbon is greater than about 0.1 percent (Schwarzenbach and Westall, 1981).

Although an equilibrium distribution between contaminant concentrations in the sorbed and aqueous phases is commonly assumed, numerous field and laboratory experiments have shown that sorption-desorption rate limitations can be significant. Sorption and desorption of hydrophobic organic compounds to sediments commonly entails an initially rapid and reversible equilibrium process, followed by slow reactions over a period of weeks or months because of relatively slow rates of mass transfer (Harmon et al., 1989; Brusseau et al., 1991). These slow reactions also result in a "desorption-resistant fraction" of contaminants that are often persistent in the environment (Carmichael et al., 1997). Several mechanisms have been suggested to account for this effect, including slow diffusion of the contaminants and absorption into solid organic matter, slow diffusion and entrapment within very small pores, and incorporation of the contaminant into natural organic matter through chemical oxidation reactions (Bosma et al., 1997).

Hydrodynamic dispersion causes a contaminant plume to spread out in directions that are longitudinal and transverse to the advective direction of ground-water flow, so that the contaminants occupy a larger volume of the aquifer than would be expected from advection. Dispersion dilutes the concentrations of contaminants by mixing with less contaminated or clean ground water. Hydrodynamic dispersion is attributed to two processes--molecular diffusion and mechanical dispersion. Molecular diffusion is the migration of contaminants along concentration gradients from zones of higher to lower concentrations. Because molecular diffusion is the dominant dispersion mechanism only at extremely low ground-water velocities, it is often ignored in ground-water studies (Davis et al., 1993). Mechanical dispersion results from local variations in flow velocity that are caused by microscopic and macroscopic heterogeneities of the porous aquifer medium (Domenico and Schwartz, 1990). Longitudinal dispersion is the spreading of a solute in a direction parallel to the direction of ground-water flow, and transverse dispersion is spreading perpendicular to the direction of ground-water flow.

### **1.3 Site/Facility Characteristics**

Background on previous studies at the freshwater tidal wetland site at West Branch Canal Creek, APG, Maryland is given here because this site was used as a baseline to compare natural attenuation measured at other wetland sites for the ESTCP study. The hydrogeology, geochemistry, biodegradation, and other natural attenuation processes were well-characterized at the APG site prior to the ESTCP study and through continuing investigations in a study separate from the ESTCP demonstration (Lorah et al., 1997; Lorah et al., in press). Background on these characteristics of the APG site are given in this section, and data collected at APG as part of the

ESTCP demonstration are discussed throughout this report. The Colliers Mills WMA site at McGuire AFB, New Jersey is described in Section 2.

### 1.3.1 Geographic Setting

The Canal Creek area of APG is near the head of the Chesapeake Bay in the Coastal Plain Physiographic Province of Maryland (Figure 1.2). The creeks and estuaries at APG are tidally influenced, and the tidal amplitude ranges from about 15 to 60 cm. Freshwater wetlands, classified as "estuarine, emergent, irregularly flooded wetlands", surround much of the West Branch Canal Creek and the reach of Canal Creek below the confluence of its two branches. Wetland areas were more extensive in the past; however, landfilling operations eliminated many wetland areas, especially along the East Branch Canal Creek (Lorah et al., 1997).

The vegetation is typical of tidal marshes in the Mid-Atlantic region. Along the eastern side of the creek, the vegetation consists largely of a monotypic stand of common reed (*Phragmites australis*), although pickerel weed is relatively common close to the creek bank. Vegetation on the western side of the creek in the study area consists of three zones - one dominated by common reed, one by southern wild rice, and one by narrow-leaf cattail. Vegetation in the wetland area does not show overt signs of stress.

### 1.3.2 Hydrogeology

The regional geology of the Canal Creek area is characterized by thick, wedge-shaped deposits of unconsolidated Coastal Plain sediments that dip southeastward. The contaminated shallow aquifer, known as the Canal Creek aquifer, is about 12 to 14 m thick near the creek and consists mainly of medium- to coarse-grained sand and gravel. The lower confined aquifer, which underlies the approximately 18 m-thick lower confining unit, is not contaminated (Lorah and Vroblecky, 1989; Lorah and Clark, 1996). The upper confining unit, Canal Creek aquifer, and lower confining unit are composed of sediments of the Cretaceous Potomac Group. Wetland sediments that overlie the Canal Creek aquifer consist of two distinct layers that have a combined thickness of about 1.8 to 3.6 m - a lower unit of silty to sandy clay or clayey sand and an upper unit of peat mixed with variable amounts of clay and silt (Lorah et al., 1997). A thin unit of sand and gravel that lies between the two wetland sediment units in the creek channel is probably a deposit from a previous channel (Figure 1.3a).

The mineralogy of the lower clayey unit of the wetland sediment consists of major amounts of quartz and minor or trace amounts of mica, feldspars, kaolinite, and siderite. The total organic carbon content in four samples from this lower unit averaged about 1 percent. The mineralogy of the upper peat unit typically consists of major amounts of quartz and organic material and minor amounts of mica, feldspars, chlorite, kaolinite, and pyrite. The total organic carbon content of the peat unit ranged from 6.9 to 32.6 percent and averaged 18 percent in 15 sediment samples (Lorah et al., 1997; Olsen et al., 1997).

Near the wetland study area along the West Branch Canal Creek, the Canal Creek aquifer is unconfined or semi-confined (Figure 1.3). The shallow ground-water flow paths are short, and most recharge and discharge is local. The general direction of flow in the aquifer is toward the West Branch Canal Creek from both sides of the creek. Recharge occurs upgradient from the

wetlands on both sides of the creek and is primarily from rainfall infiltration. Ground-water-flow directions within the wetland area are predominantly upward, with water from the Canal Creek aquifer discharging through the wetland sediments and the creek bank and bottom sediments. Reversals in ground-water flow directions are evident at high tide in some places. The average linear ground-water flow velocity in the wetland sediments is estimated to be about 0.6 to 0.9 m/yr from flow-net analysis of ground-water head data (Lorah et al., 1997).

### 1.3.3 Ground-water Contamination

About 100 piezometers, located in clusters with 15-cm screened intervals in the wetland sediment and aquifer, were used to characterize the ground-water contamination in the wetland study area between 1995-99 (Lorah et al., 1997). Porous membrane samplers, called "peepers", that collect ground water by diffusion also were used to obtain samples from 2.5-cm intervals in the upper 60 cm of the wetland sediment. TCE, 1,1,2,2-tetrachloroethane (PCA), carbon tetrachloride, and chloroform, were the four major contaminants present in ground water in the Canal Creek area that were known to have direct sources from use and disposal (Lorah and Clark, 1996). TCE (Figure 1.4) and PCA (data not shown) had similar distributions along the southern A-A' transect through the wetland, with the highest concentrations upgradient from the eastern edge of the wetland at CC-27A and spreading downgradient predominantly in two fingers that remain shallow in the aquifer. Downward transport of the contaminants in the aquifer at site CC-27, which is near a suspected source from a past sewer line discharge point (Lorah et al., 1997), could have been partly impeded by the clayey silt layer below the screen in CC-27A. The fact that the contaminants then remain shallow in the aquifer in the wetland area probably reflects the upward component of ground-water flow. Although concentrations of PCA (about 4,000 µg/L) were an order of magnitude higher than TCE (about 300 µg/L) near the suspected source by site CC-27, their concentrations were similar downgradient in the aquifer along A-A'. Concentrations of TCE and PCA were each in the range of 100 to 300 µg/L in a thin zone that lies directly beneath the wetland sediments (Figure 1.4). The TCE and PCA plumes along section A-A' extend to the western side of the creek channel, which confirms measurements of hydraulic-head gradients that indicated a lateral component of ground-water flow in the aquifer beneath the creek and discharge to wetland sediments on the western side of the channel along this section (Figure 1.3A).

Concentrations of VOCs decreased substantially, however, along the upward direction of flow through the overlying wetland sediments on both sides of the creek (Figure 1.4). Concentrations of TCE were in the range of 50 to 100 µg/L in the lower clayey unit of the wetland sediments and decreased to about 5 µg/L at the base of the upper peat unit. TCE concentrations were below the detection limit of 0.2 µg/L within 0.9 m below land surface (Figure 1.4).

PCA was the major contaminant in the ground water along transect C-C', occurring at a maximum concentration of about 2,000 µg/L in the aquifer at sites WB-32 and WB-33 at the eastern edge of the wetland (Figure 1.5). Unlike section A-A', where both PCA and TCE were major ground-water contaminants, TCE concentrations were much lower than PCA



concentrations in the aquifer and wetland sediment along section C-C'. TCE concentrations were a maximum of 54 µg/L at site WB-32 and decreased downgradient to less than about 20 µg/L at all piezometers within the wetland area (Lorah et al., 1997). As observed along section A-A', the PCA plume along section C-C' was primarily in the shallow region of the aquifer and had an upward trend into the wetland sediments (Figure 1.5). The maximum PCA concentration in water in the wetland sediment (300 µg/L) was measured in WB-35B, which is screened near the base of the upper peat unit. In contrast to section A-A', the contaminant plume does not appear to reach the creek channel or the western side of the creek along section C-C'. Next to the creek channel (site WB-37), PCA was less than 2.0 µg/L, except in one piezometer (WB-37C) screened immediately below the wetland sediment (Figure 1.5). The PCA distribution, therefore, was consistent with the head distributions, which indicated that the area around sites WB-35 and WB-36 was a focused discharge area at high tide (Figure 1.3B). Even in this focused discharge area, PCA concentrations decreased greatly along the upward direction of flow in the wetland sediments. PCA concentrations were more than two orders of magnitude lower in water from the piezometer screened about 0.3 m above WB-35B (WB-35A) (Figure 1.5).

#### 1.3.4 Evidence of Biodegradation in Wetland

The distributions of redox-sensitive constituents show that anaerobic conditions favorable for reductive dechlorination of the chlorinated VOCs are present in the wetland sediments, whereas biodegradation would not be expected to be a significant attenuation process under the generally aerobic conditions in the aquifer (Lorah et al., 1997). Iron-reducing conditions, characterized by Fe(II) concentrations greater than 1,000 µg/L, were predominant in the lower clayey unit of the wetland sediment (Figures 1.6 and 1.7). Methanogenic conditions characterized the ground water in the upper peat unit, although relatively high concentrations of Fe(II) and sulfide were present in some samples collected from this unit (Figures 1.6 and 1.7).

Relatively high concentrations of the parent compounds TCE and PCA were measured in the aquifer, whereas concentrations of daughter products were low or undetectable. In contrast, concentrations of the parent compounds were low, or in many cases, undetectable in the more reducing environment of the wetland sediments, and possible daughter products were present in relatively high concentrations (Figures 1.6 and 1.7). Figures 1.6 and 1.7 show the vertical changes in the relative concentrations of parent and daughter compounds with depth in the aquifer and wetland sediments, using results from site WB-26 along section A-A' and from site WB-35 along section C-C'. Similar vertical profiles were observed at all contaminated sites for the two transects in the wetland. The daughter products that were observed in the highest concentrations in most of the piezometers screened in the wetland sediment were 12DCE (total of *cis*- and *trans*-12DCE) and vinyl chloride (VC). These daughter products could be produced from TCE biodegradation by hydrogenolysis and from PCA degradation through hydrogenolysis and dichloroelimination pathways (Lorah et al., 1997; Lorah and Olsen, 1999a). The daughter products 112TCA and 12DCA, which can be produced by hydrogenolysis of PCA, also were commonly observed in the anaerobic wetland sediments but generally not in concentrations as high as those observed for 12DCE and VC. Total concentrations of the parent and daughter

compounds decreased along the upward flow path through the wetland sediment until they were below detection within 0.15 to 0.30 m below land surface (Figures 1.6 and 1.7). The upward decrease in concentrations of TCE and PCA, and the concomitant increase in concentrations of possible anaerobic daughter products, provide strong evidence that biodegradation is occurring as ground water flows through the anaerobic wetland sediments.

### 1.3.5 Physical natural attenuation processes

Volatilization was shown to be an insignificant transport mechanism for the volatile contaminants in the wetland study area by using sulfur hexafluoride as a conservative gas in a ground-water tracer test (Olsen and Johnson, 2002). Equilibrium sorption isotherms were measured in 24-hour batch tests with the wetland sediment (Lorah et al., 1997). The distribution coefficients ( $K_d$ 's) were estimated to describe the ratios of sorbed to aqueous concentrations of PCA and the daughter products *cis*-12DCE, *trans*-12DCE, and VC. The estimated  $K_d$ 's for PCA, *cis*-12DCE, *trans*-12DCE, and VC were about 2.3, 1.8, 2.4, and 1.3 liters per kilogram of sediment, respectively (Lorah et al., 1997). Sorbed concentrations of PCA, *cis*-12DCE, and *trans*-12DCE in the wetland sediments, therefore, would be expected to be about twice the concentration measured in the water, whereas sorbed concentrations of VC would not be much greater than the aqueous concentrations. Coefficients of retardation, which were calculated using the  $K_d$ 's and an advective flow velocity of about 0.6 m/yr, indicated that sorption alone would cause the movement of the contaminants in the wetland sediments to be 6 to 10 times slower than the advective ground-water flow (Lorah et al., 1997).

### 1.3.6 Surface Water

Chemical analyses of 120 samples collected from the West Branch Canal Creek between June 1995 and March 1996 show that the surface water is freshwater to slightly brackish (Olsen et al., 1997). The minimum, median, and maximum total dissolved solids (TDS) concentrations in West Branch Canal Creek were 152, 1,600 and 4,000 mg/L, respectively. Freshwaters are characterized as having TDS less than about 1,000 mg/L; brackish waters in the range of about 1,000 to 20,000 mg/L; and saline water as equal or greater than 35,000 mg/L (Drever, 1988).

VOCs have been detected in surface-water samples from West Branch Canal Creek, but measured concentrations are low (Lorah and Clark, 1996). The maximum concentrations of VOCs measured in the West Branch Canal Creek in 1988-89 were 19 µg/L of carbon tetrachloride and 23 µg/L of chloroform (Lorah and Clark, 1996). More extensive surface-water sampling along the West Branch Canal Creek during 1999-2000 showed a maximum VOC concentration of 50 µg/L, and chloroform and carbon tetrachloride were detected most frequently (Phelan et al., 2001a). A newly identified plume of VOCs (Phelan et al., 2001b), located a little south of the A-A' transect and centered beneath the West Branch Canal Creek, is believed to be a major source of the chloroform and carbon tetrachloride to the surface water (Phelan et al., 2001a).

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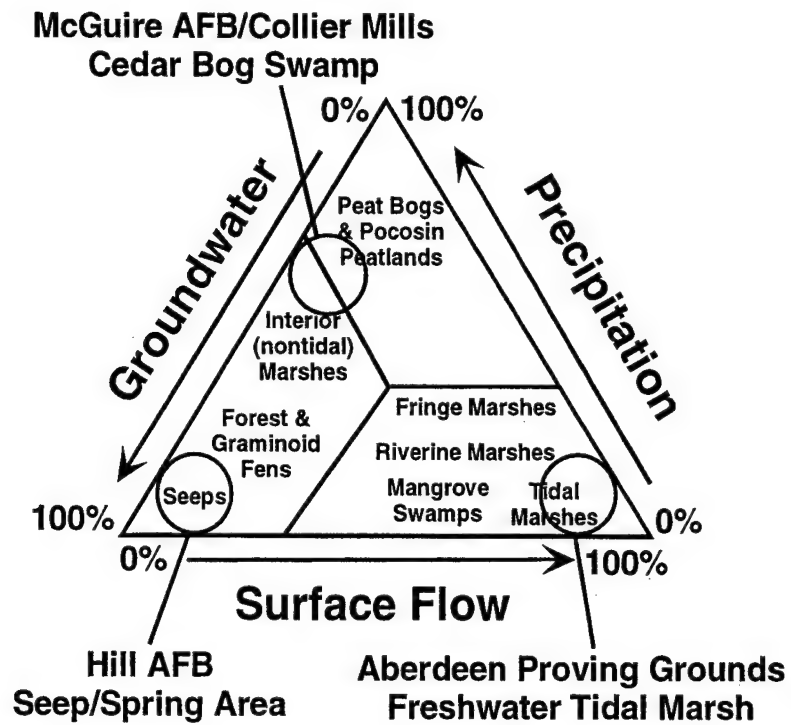


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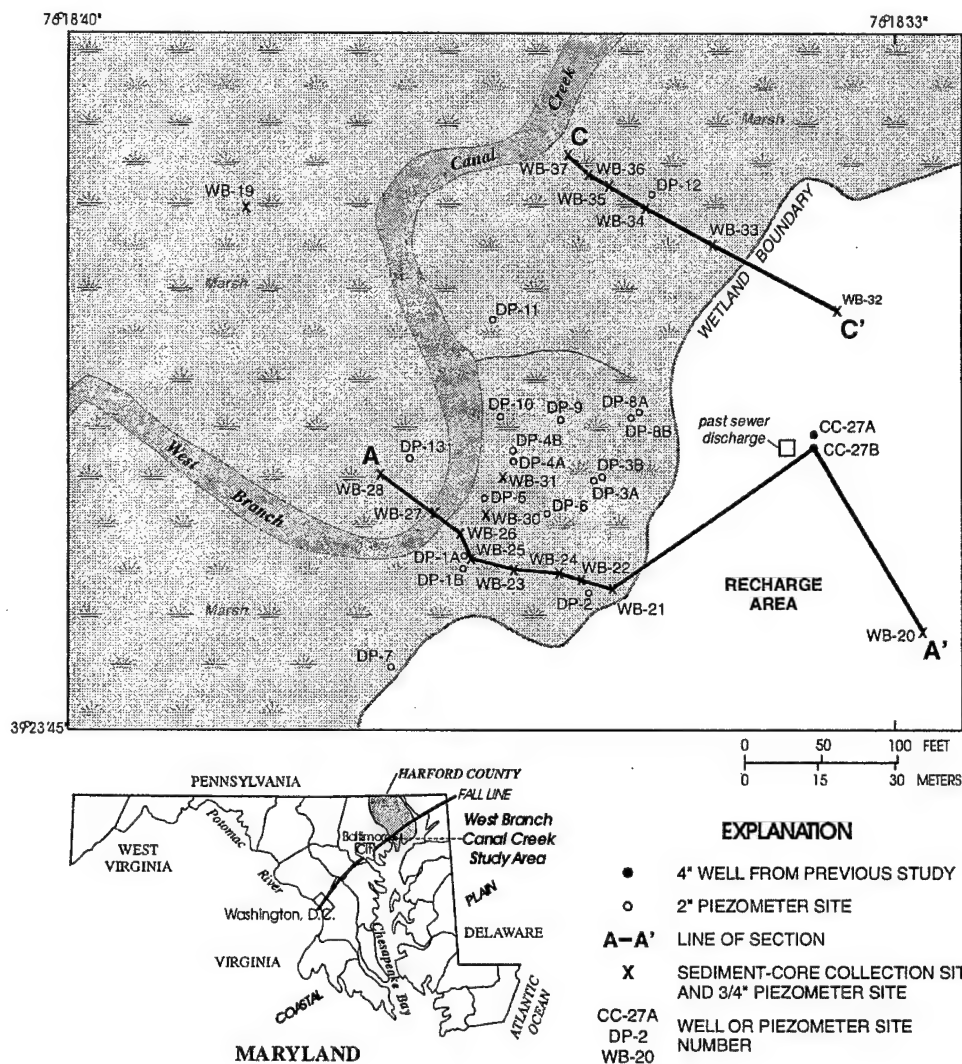
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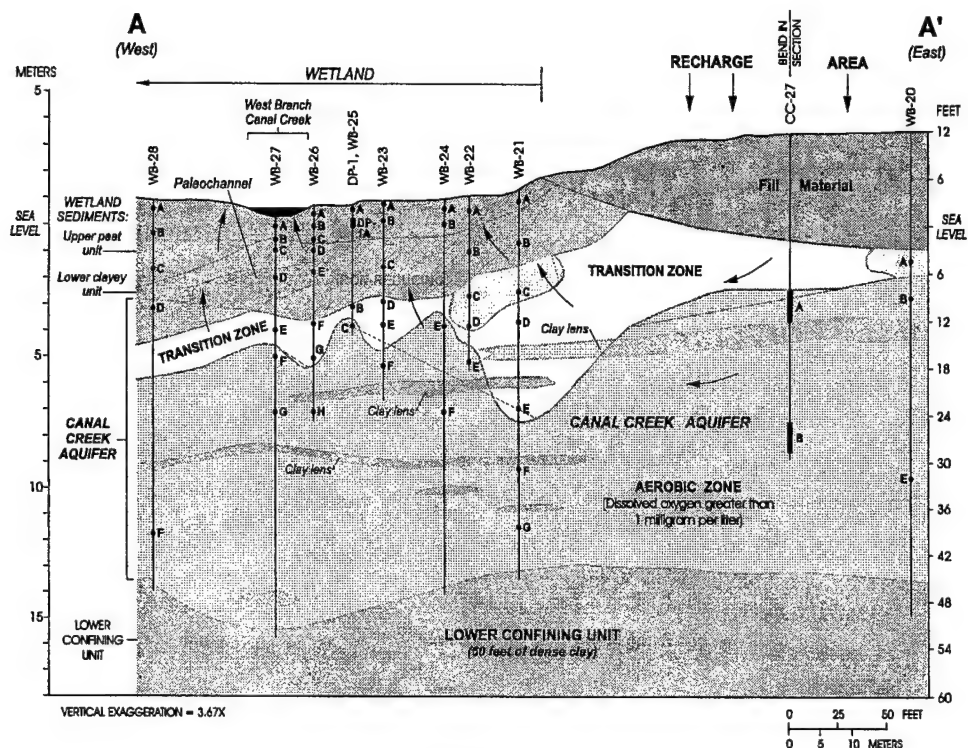
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**Figure 1.1.** Classification of wetland study areas according to relative importance of water source (modified from Richardson (1999) and Brinson (1993)).

**Figure 1.2.** Location of the West Branch Canal Creek wetland site, Aberdeen Proving Ground, Maryland, and the locations transects A-A' and C-C'. (From Lorah and Olsen, 1999b)





#### EXPLANATION

A • PIEZOMETER SCREEN

← GROUND-WATER-FLOW DIRECTION AT LOW TIDE

□ TRANSITION ZONE – Concentrations of dissolved oxygen less than 1.0 milligrams per liter; concentrations of iron, sulfide, and methane less than those observed in anaerobic zones.

#### ANAEROBIC ZONES:

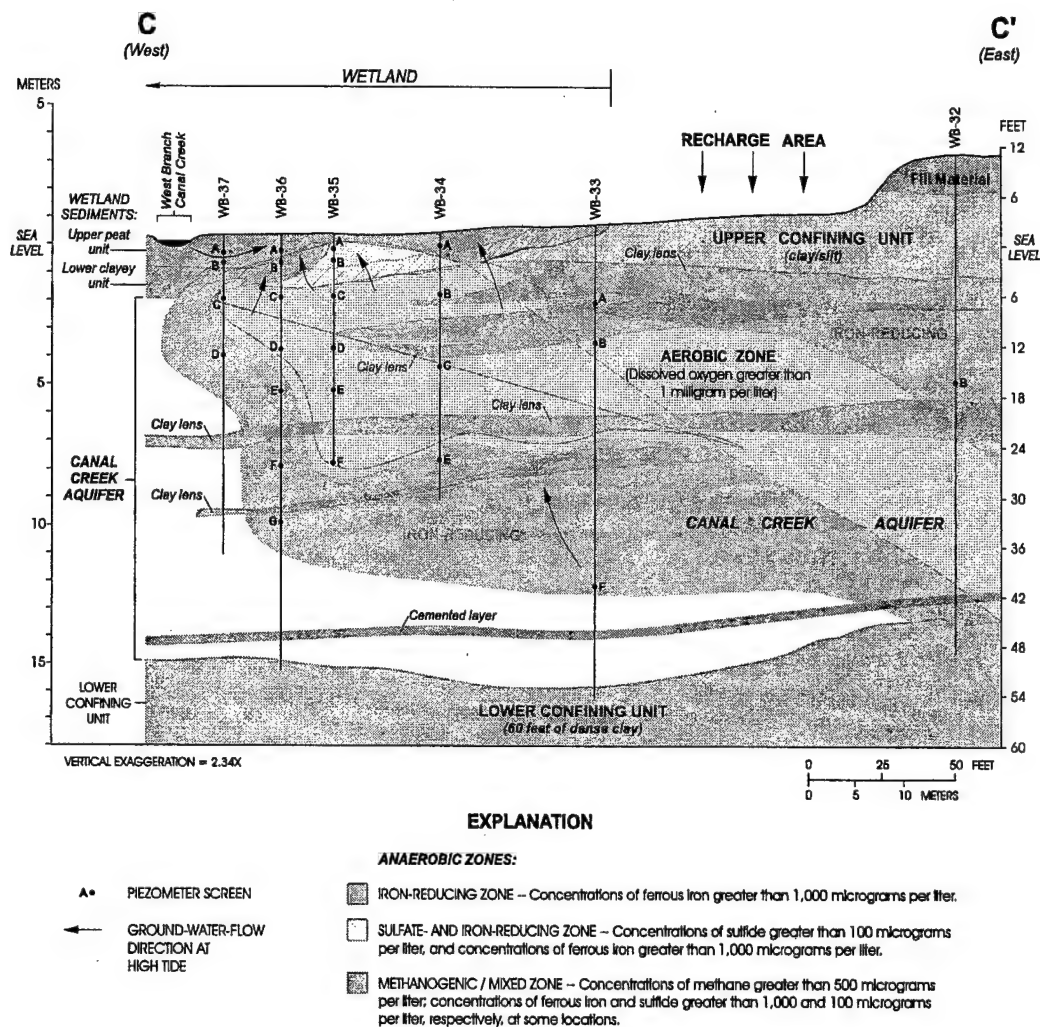
■ IRON-REDUCING ZONE – Concentrations of ferrous iron greater than 1,000 micrograms per liter.

□ SULFATE-REDUCING ZONE – Concentrations of sulfide greater than 100 micrograms per liter.

■ METHANOGENIC / MIXED ZONE – Concentrations of methane greater than 500 micrograms per liter; concentrations of ferrous iron and sulfide greater than 1,000 and 100 micrograms per liter, respectively, at some locations.

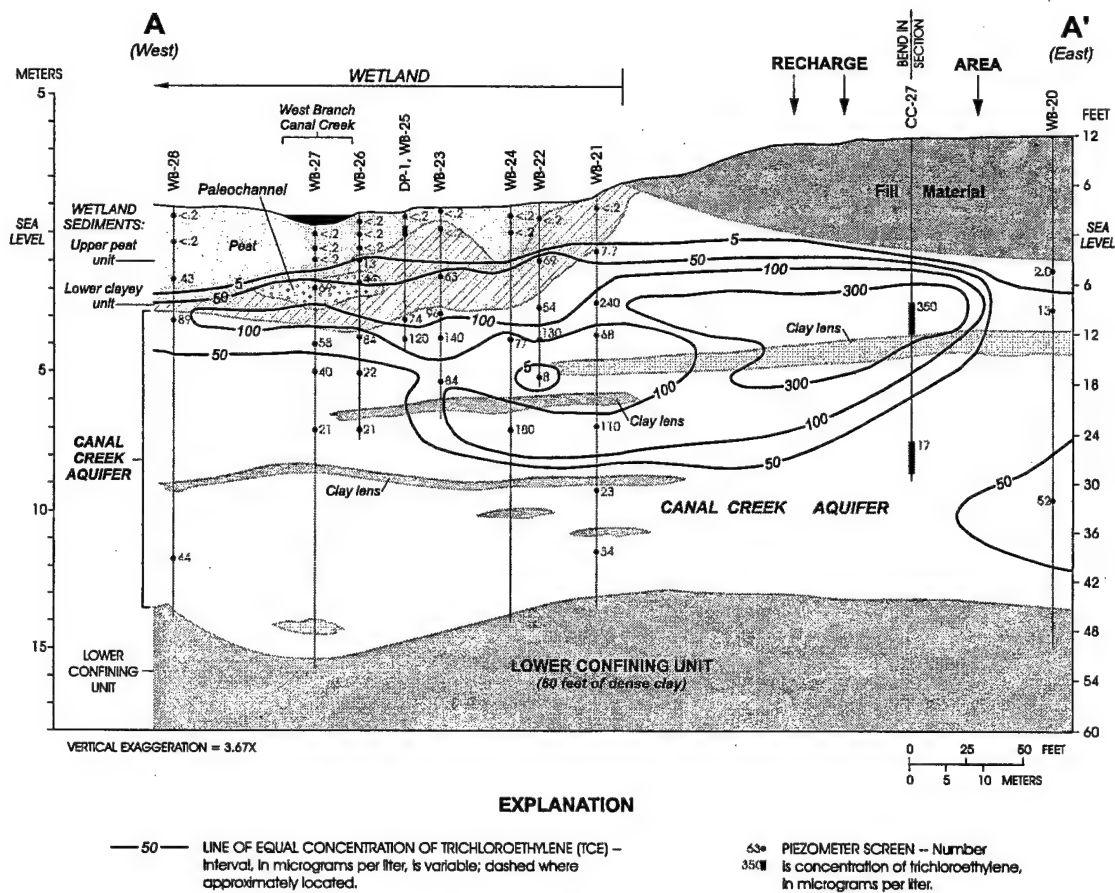
**Figure 1.3A.** Section (A) A-A' and (B) C-C' through the wetland field site showing the hydrogeology, locations of piezometer screens, and predominant redox zones in ground water during September-October 1995. Data from peepers that were placed 0 to 0.61 m below land surface at sites WB-24, WB-25, WB-26, WB-34, WB-35, WB-36, and WB-37 also were used to delineate redox zones. (From Lorah et al., 1997)



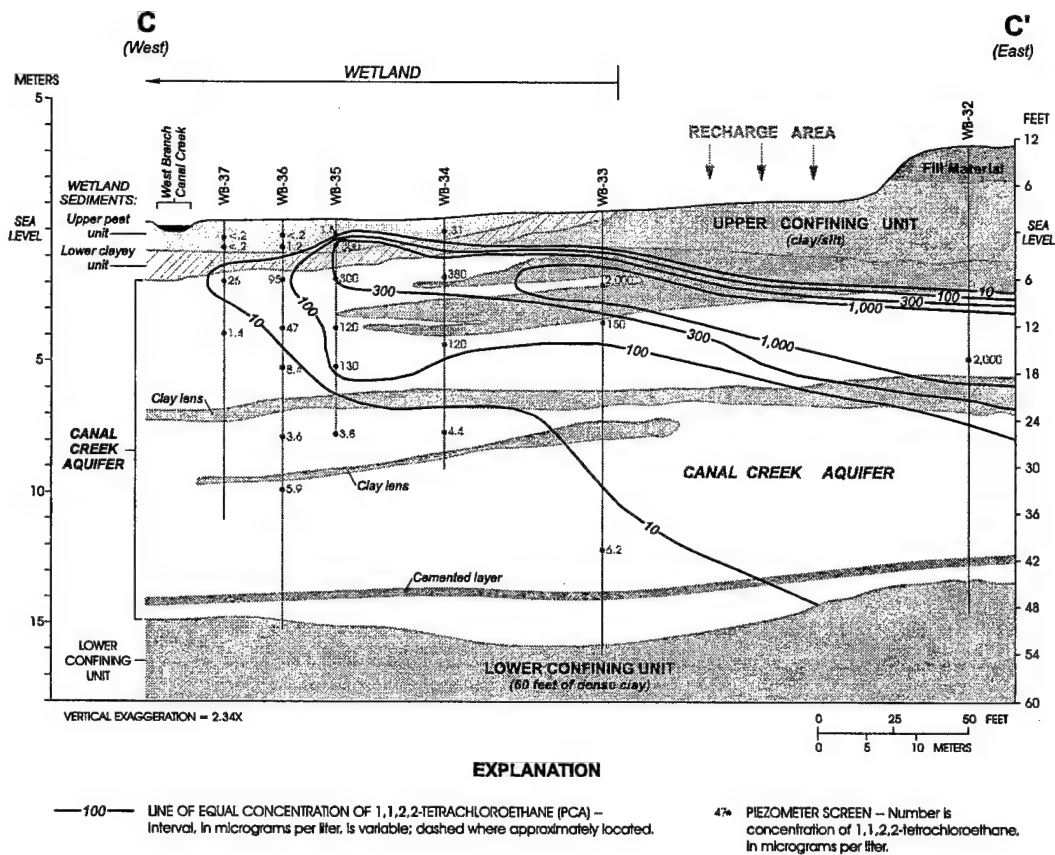


**Figure 1.3B.** Section C-C' through the wetland field site showing the hydrogeology, locations of piezometer screens, and predominant redox zones in ground water during September-October 1995. Data from peepers that were placed 0 to 0.61 m below land surface at sites WB-24, WB-25, WB-26, WB-34, WB-35, WB-36, and WB-37 also were used to delineate redox zones. (From Lorah et al., 1997)

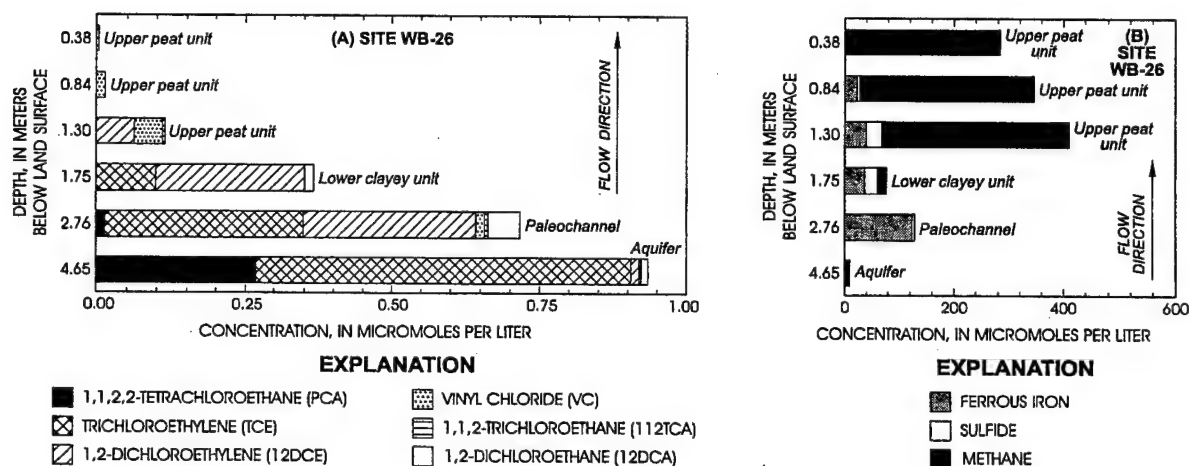




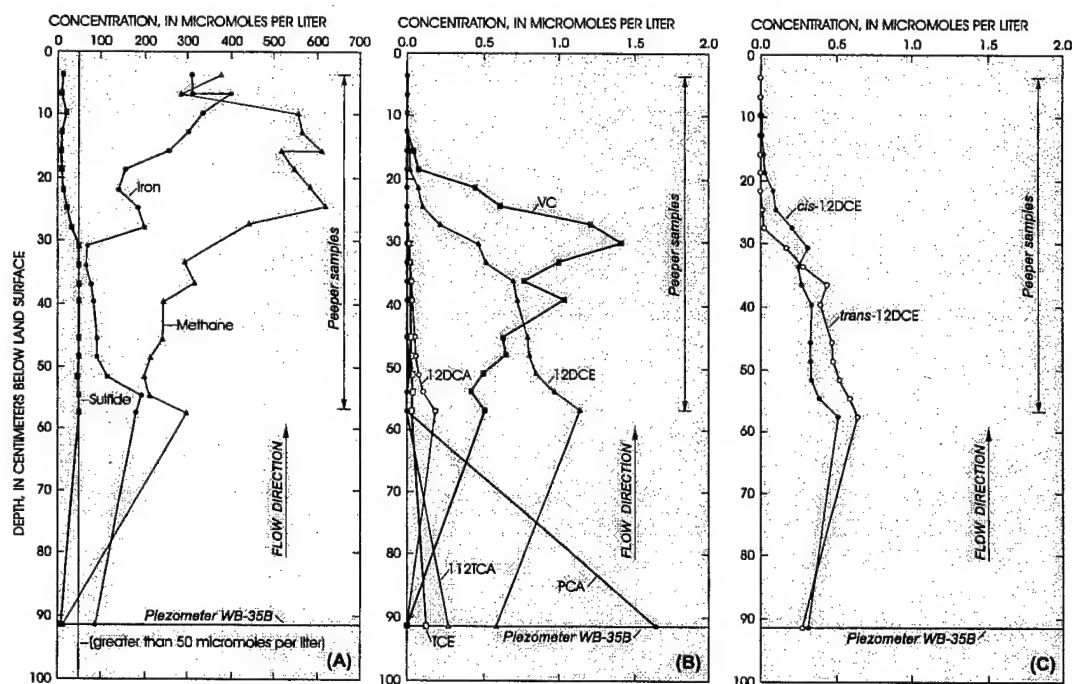
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(From Lorah et al., 1997)



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(From Lorah et al., 1997)



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**Section 2. Natural attenuation of chlorinated solvents in a forested swamp (Colliers Mills Wildlife Management Area, New Jersey) and comparison to a freshwater tidal wetland (Aberdeen Proving Ground, Maryland)**

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## **Section 2. Natural Attenuation of Chlorinated Solvents in a Forested Swamp (Colliers Mills Wildlife Management Area, New Jersey) and Comparison to a Freshwater Tidal Wetland (Aberdeen Proving Ground, Maryland)**

### **2.1 Introduction**

The former Boeing Michigan Aeronautical Research Center (BOMARC) Missile Facility, McGuire AFB, NJ/Colliers Mills Wildlife Management Area wetland site, which will be referred to as the Colliers Mills WMA site, was selected as one of the three demonstration sites for this ESTCP study (Figure 2.1). The basic approach taken by this demonstration was to implement key methodologies needed to evaluate natural attenuation at wetland discharge sites, including installation of multilevel piezometer (or other ground-water sampler) transects; determination of ground-water flow paths and rates; determination of redox zones; evaluation of biodegradation by determining levels of parent contaminants, reactive intermediates and non-toxic end products; and evaluation of other possible major natural attenuation processes. The efficiency of natural attenuation (the relative rate and completeness of transformation of the contaminants) in the forested swamp at Colliers Mills WMA site is evaluated and compared to the APG tidal freshwater wetland site along the West Branch Canal Creek (Figure 1.2). TCE is the major contaminant in the plume discharging to the Colliers Mills WMA wetland site (Tetra Tech, 1999), whereas TCE and PCA are the major contaminants at the APG site (see Section 1 for background on the APG site).

#### **2.1.1 Purpose and scope**

The objectives of this demonstration were to assess the extent of chlorinated solvent natural attenuation at the Colliers Mills WMA site and to compare the results of this study to chlorinated solvent natural attenuation at the West Branch Canal Creek, APG site. Colliers Mills WMA is an inland forested swamp or bog that appears to be ground water and precipitation dominated. The Aberdeen Proving Ground site is a freshwater tidal wetland where surface water is a dominant water source (Figure 1.1). Whereas the vegetation at the APG site consists primarily of *Phragmites*, or common reed, the Colliers Mills WMA site consists of sphagnum moss, shrubs, and cedar trees. The wetland vegetation, sediment, hydrology, and water chemistry at the Colliers Mills WMA and APG sites are very different, although the underlying contaminated aquifers at both sites consist of unconsolidated Coastal Plain sands. Comparison of these wetland sites will allow an assessment of characteristics affecting the efficiency of natural attenuation of chlorinated solvents. Although reconnaissance activities at the Colliers Mills WMA wetland site indicated less efficient degradation than at the APG site, it was selected as a



demonstration site to gain a better understanding of factors limiting the natural attenuation of chlorinated solvent plumes discharging into wetlands.

### **2.1.2 Description of Field Site**

The BOMARC Missile Facility and McGuire AFB are located in south-central New Jersey, midway between Philadelphia, PA, and the Atlantic Ocean (Figure 2.1). The BOMARC Missile site is an inactive facility on 218 acres of rural land leased from U.S. Army Fort Dix Military Reservation and located approximately 11 miles east of McGuire AFB. The BOMARC Missile Facility was constructed in the mid-1950's to early 1960 and was deactivated in 1972, although it remains under Air Force lease and jurisdiction. The BOMARC missiles were housed in individual launcher shelters, which now are in general disrepair and surrounded by overgrown vegetation. TCE utilization or storage at the BOMARC Missile Site has not been documented, although it was commonly used as a degreaser for metal parts cleaning. The area surrounding the Missile Site is undeveloped and mostly forested (Figure 2.2).

The wetland field site for this demonstration is situated outside the eastern boundary of the BOMARC Missile facility, partially overlapping the area where a TCE plume was previously defined (Tetra Tech, 1999) and continuing northeast into the Colliers Mills WMA (Figures 2.2 and 2.3). The Colliers Mills WMA is owned by the New Jersey Department of Natural Resources and managed by the New Jersey Pinelands Commission. Colliers Mills WMA is in the northeast corner of the New Jersey Pinelands, also known as the Pine Barrens, which is an expansive, relatively level, wooded area covering about 2000 square miles on the Coastal Plain physiographic province (TetraTech, 1999). The Pinelands consist primarily of coniferous forest, which differs ecologically from the surrounding deciduous forest climax vegetation that is more typical of the eastern United States. The Pinelands has been designated as a natural preserve and, consequently, has severe restrictions on development and use. The Colliers Mills WMA is a scrub pine forest that is dominated by stands of mature cedars; deciduous trees with dense underbrush surround the pine forest. Much of the forest floor in the study site consists of spongy peat and small pools of standing water. The Elisha Branch and Success Branch of the Toms River lie southeast of BOMARC Missile Site and flow northeasterly through the Colliers Mills WMA (Figure 2.2). Flow in Elisha Branch is intermittent, and a defined creek channel commonly is not evident until it joins Success Branch. The study area lies within the Coastal Plain Physiographic Province and is characterized by low elevation and relief, both of which generally decrease from northwest to southeast toward the New Jersey coastline. The Kirkwood-Cohansey aquifer system is an unconfined aquifer of Tertiary and Cretaceous age that underlies the Colliers Mills WMA and is the principal source of potable water in the study area (Zapeczka, 1989).

### **2.1.3 Previous Investigations**

Previous site investigations were performed at the BOMARC Missile site and did not include collection of ground-water samples within the Colliers Mills WMA (Tetra Tech, 1999). Initial site investigations conducted in 1984 and 1986 were focused on radioactive contaminants released in 1960 during a non-nuclear fire and explosion at the BOMARC Missile site. In 1992, a Record of Decision (ROD) was signed to implement a remedial design to excavate, containerize, transport and dispose of any radioactive contamination that resulted from the 1960



fire and explosion. In 1987, VOC contamination was identified in the ground water at the BOMARC Missile site. A remedial investigation determined the existence of a TCE plume within the ground water that was moving from the BOMARC Missile site in an easterly direction toward Colliers Mills WMA and the Naval Air Engineering Station, Lakehurst, NJ.

In 1995, Tetra Tech, Inc. began a remedial investigation/feasibility study (RI/FS) investigation [later changed to an Engineering Evaluation/Cost Analysis (EE/CA) investigation] of the TCE plume at the BOMARC Missile Site. Upgradient of the wetland area, Tetra Tech (1999) observed two distinct sand layers, an upper 7.6- to 15-m thick strata of tan/orange coarse to fine sand and an underlying 3.0- to 11-m thick strata of dark gray/brown fine sand with minor amounts of silt. An organic silt/peat strata that ranged in thickness from about 0.61 to 3.0 m is located between the two sand units. Tetra Tech collected ground-water samples from 3.0-m depth intervals in Hydropunch borings in 1995 and 1997 upgradient of the wetland area by the BOMARC facility (Figure 2.2 and 2.4). TCE was detected in 83 and 92 percent of the samples in 1995 and 1997, respectively, and concentrations were as high as 6,400  $\mu\text{g/L}$ . Total 1,2-dichloroethene (12DCE) was detected in 10 to 15 percent of the samples, and concentrations were as high as 54  $\mu\text{g/L}$ . 11DCE was detected infrequently in concentrations below 0.5  $\mu\text{g/L}$  (Tetra Tech, 1999). Analyses for vinyl chloride (VC) were conducted in 1997, but it was not detected. The highest concentrations of TCE and 12DCE in Hydropunch borings were obtained from 11 to 20 m below ground surface (bgs) (Figure 2.4). In 1998, Tetra Tech installed ground-water monitoring wells ("MW" sites in Figure 2.2 and 2.3). TCE concentrations from these monitoring wells and in the Hydropunch samples showed that the TCE plume was much larger than thought from previous investigations. TCE concentration was highest in MW-10 (420  $\mu\text{g/L}$ ) (Figure 2.3). Vertical delineation of the plume was difficult from these monitoring wells because of the long, varying screened intervals that were used [3.0- to 4.6-m screened intervals, Tetra Tech (1999)]. Tetra Tech (1999) concluded that the TCE plume discharges into Elisha and Success Branch based on solute transport model results. Tetra Tech (1999) determined that ground-water-flow directions in the plume at the BOMARC site was predominantly to the northeast and estimated that the flow velocity in the aquifer was about 0.15 m/day.

## **2.2 Materials and Methods**

Methods are given here for characterization of natural attenuation at the Colliers Mills WMA. For comparison to the West Branch Canal Creek wetland area at APG, results are used from earlier investigations (see Section 1) or from piezometers and porous membrane sampling devices (peepers) sampled in 2000 using the same methods as those published earlier (Lorah et al., 1997; Olsen et al., 1997; Lorah and Olsen 1999a,b; Spencer et al, in press).

### **2.2.1 Monitoring Network**

Multi-level transects and small-scaled vertical definition of ground-water chemistry are needed to evaluate natural attenuation in wetlands. Drive-point piezometers and peepers were used to establish a monitoring network in the Colliers Mills WMA, as was used previously at the West Branch Canal Creek APG site (Lorah et al., 1997; Lorah and Olsen, 1999b). The piezometer monitoring network at the Colliers Mills WMA was installed primarily during a reconnaissance phase effort in November 1999 (Table 2.1). The purpose of the reconnaissance effort was to (1) determine if the TCE plume previously identified in upland areas at the site

discharged to the wetland and creek-bottom sediments, (2) determine a major ground-water flowpath for the contaminants through the wetland area, and (3) gather initial evidence of natural attenuation of the TCE in the wetland and creek-bottom sediments. The reconnaissance effort began on November 5-12, 1999, with clearance of paths through the wetland, installation of piezometers, and collection of ground-water and surface-water samples. During December 6-10, 1999, ground-water sample collection was continued, and surveying was done to determine elevations and locations of the newly installed piezometers.

Table 2.1. Piezometer construction data for Colliers Mills WMA wetland site, New Jersey.  
[Piezometers with "T" in the name are temporary piezometers made of PVC; all others are steel.  
Piezometer screens are 0.15 m long. LS, land surface; TOC, top of casing; --, not measured.  
Elevations are relative to mean sea level; depths are relative to land surface.]

Piezometer name	Elevation at TOC (ft)	Elevation at TOC (m)	Lithologic unit	Depth to screen bottom (ft)	Depth to screen bottom (m)	Casing stick-up length (ft)	Casing stick-up length (m)
CM1-1.5T	126.44	38.54	peat	1.5	0.46	1.55	0.47
CM1-12	127.34	38.81	aquifer	12.0	3.66	2.43	0.74
CM2-1T	125.14	38.14	peat	1.0	0.30	2.45	0.75
CM2-1.5T	125.81	38.35	peat	1.5	0.46	1.55	0.47
CM2-5	126.65	38.60	aquifer	5.0	1.52	2.60	0.79
CM2-12	126.65	38.60	aquifer	12.0	3.66	2.34	0.71
CM3-0.7	123.26	37.57	peat	0.7	0.21	2.61	0.80
CM3-1.5T	123.26	37.57	peat	1.5	0.46	2.53	0.77
CM3-8	123.43	37.62	aquifer	8.0	2.44	2.70	0.82
CM3-12	123.03	37.50	aquifer	12.0	3.66	2.30	0.70
CM3-16 <sup>a</sup>	122.03	37.19	aquifer	16.0	4.88	1.30	0.40
CM3-31 <sup>a</sup>	122.86	37.45	aquifer	31.0	9.45	2.13	0.65
CM3-33 <sup>a</sup>	122.68	37.39	aquifer	33.0	10.06	1.95	0.59
CM4-1.5T	122.53	37.35	peat	1.5	0.46	1.95	0.59
CM4-12	122.86	37.45	aquifer	12.0	3.66	2.27	0.69
CM4-17 <sup>a</sup>	121.49	37.03	aquifer	17.0	5.18	0.91	0.28
CM4-34 <sup>a</sup>	122.80	37.43	aquifer	34.0	10.36	2.22	0.68
CM5-1.6T	127.00	38.71	peat	1.6	0.49	1.60	0.49
CM5-12	127.80	38.95	aquifer	12.0	3.66	2.50	0.76
CM6-12	125.74	38.33	aquifer	12.0	3.66	2.40	0.73
CM7-12	126.13	38.44	aquifer	12.0	3.66	2.20	0.67
CM8-5	127.49	38.86	aquifer	5.0	1.52	2.45	0.75
CM9-1T	123.41	37.61	peat	1.0	0.30	2.19	0.67
CM9-3T	123.65	37.69	peat	3.0	0.91	2.88	0.88
CM9-5	125.01	38.10	aquifer	5.0	1.52	2.42	0.74
CM9-10.5	123.10	37.52	aquifer	10.5	3.20	2.21	0.67
CM9-21	123.12	37.53	aquifer	21.0	6.40	2.15	0.66
CM9-33 <sup>a</sup>	125.01	38.10	aquifer	33.0	10.06	1.80	0.55
CM10-0.5T	123.45	37.63	peat	0.5	0.15	2.77	0.84
CM10-12	123.00	37.49	aquifer	12.0	3.66	2.40	0.73
CM10-20	123.01	37.49	aquifer	20.0	6.10	2.40	0.73

CM11-1T	122.45	37.32	peat	1.0	0.30	2.32	0.71
CM11-12	122.72	37.40	aquifer	12.0	3.66	2.32	0.71
CM11-20	122.53	37.35	aquifer	20.0	6.10	2.45	0.75
CM12-1T	122.17	37.24	peat	1.0	0.30	2.50	0.76
CM12-12	122.48	37.33	aquifer	12.0	3.66	2.75	0.84
CM12-23	122.12	37.22	aquifer	23.0	7.01	2.45	0.75
CM13-1T	121.60	37.06	peat	1.0	0.30	2.50	0.76
CM13-2T	120.70	36.79	peat	2.0	0.61	1.60	0.49
CM13-12	121.96	37.17	aquifer	12.0	3.66	2.93	0.89
CM13-21	122.35	37.29	aquifer	21.0	6.40	3.31	1.01
CM14-2T	120.84	36.83	peat	2.0	0.60	1.50	0.46
CM14-5	121.75	37.11	aquifer	5.0	1.52	2.40	0.73
CM15-1T	122.32	37.28	peat	1.0	0.30	3.18	0.97
CM15-12	122.44	37.32	aquifer	12.0	3.66	2.54	0.77
CM16-1T	126.89	38.68	peat	1.0	0.30	1.83	0.56
CM16-2	126.97	38.70	peat	2.0		2.00	0.61
CM16-10	127.57	38.88	aquifer	10.0	3.05	2.40	0.73
CM16-12	127.94	39.00	aquifer	12.0		2.88	0.88
CM16-28	126.66	38.61	aquifer	28.0	8.53	1.60	0.49
CM17-0.5T	129.02	39.32	peat	0.5	0.15	3.10	0.94
CM17-12	128.52	39.17	aquifer	12.0	3.66	2.45	0.75
CM17-23	128.11	39.05	aquifer	23.0	7.01	2.02	0.62
CM17-51 <sup>a</sup>	128.66	39.22	aquifer	51.0	15.54	2.60	0.79
CM18-16 <sup>a</sup>	--	--	aquifer	16.0	4.88	2.53	0.77
CM18-55 <sup>a</sup>	--	--	aquifer	55.0	16.76	2.60	0.79

#### Streambed Piezometers

ST1-1	--	--	peat	1.0	0.30	4.45	1.36
ST1-3	--	--	aquifer	3.0	0.91	4.27	1.30
ST2-1	--	--	peat	1.0	0.30	4.10	1.25
ST2-3	--	--	aquifer	3.0	0.91	4.72	1.44
ST3-1	--	--	peat	1.0	0.30	4.62	1.41
ST3-4	--	--	aquifer	4.0	1.22	4.66	1.42
ST4-2	--	--	aquifer	2.0	0.61	2.55	0.78
ST4-3	--	--	aquifer	3.0	0.91	1.67	0.51
ST5-3	--	--	aquifer	3.0	0.91	3.20	0.98
ST6-3	--	--	aquifer	3.0	0.91	3.15	0.96
SWB-1T	--	--	peat	1.0	0.30	4.85	1.48
SWB-3T	--	--	aquifer	3.0	0.91	2.70	0.82

<sup>a</sup> Piezometers installed in second drilling effort in December 2000-March 2001.

Approximately 42 drive-point piezometers were installed in the wetland in clusters at 17 sites, designated as "CM" (Figures 2.3, 2.5, and 2.6). Individual piezometers were noted by the site name followed by a dash and a number that indicates the approximate depth (in feet below land surface) of the bottom of the screened interval (for example, "CM9-21" indicates a piezometer screened at a depth of about 21 ft at site CM9). Depths in meters also are indicated in Table 2.1. Additional drilling was done during December 2000-March 2001 to install deeper piezometers and to obtain sediment cores for lithologic description (Table 2.1). Because of logistical difficulties, only 9 of the planned 20 additional piezometers were installed during this second drilling effort. Site CM18 was the only new site; the remaining piezometers were placed to obtain deeper samples at existing sites (Table 2.1).

For monitoring network installation during the reconnaissance effort, the probable direction of movement of the TCE ground-water plume as it migrated from the BOMARC Missile site toward the Colliers Mills WMA was inferred from the Tetra Tech (1999) data. Piezometer sites CM1 to CM7, CM9, and CM15 (Figure 2.5) were placed approximately 15 m into the wetland along the wetland boundary in the inferred area of plume migration. The wetland boundary was determined by vegetation type and the presence of moist soil within about 5.1 to 7.6 cm of land surface. To guide placement of the piezometers in November 1999, samples for volatile organic compounds (VOCs) were collected immediately after piezometer installation and analyzed in the field within an hour of collection using a direct-sampling ion-trap mass spectrometer. After locating the area of highest measured VOC concentrations in the shallow aquifer along the wetland boundary, piezometers were installed along a northeast transect, which is the reported general direction of ground-water flow in the aquifer (Tetra Tech, 1999), to Success Branch (Figure 2.5 and 2.6). Surface-water samples also were collected and analyzed in the field for VOCs to assist in placement of the piezometer transect to the stream (Figure 2.6).

Piezometers with screen depths greater than 1.2 m are screened in the aquifer and required a gas-powered Cobra hammer for emplacement. These piezometers were constructed of threaded 1.5 m-lengths of 0.019-m inside diameter (i.d.) black iron and of 0.15-m long screened intervals made of stainless-steel mesh with 100 micrometer pore diameter. Drive points for these piezometers were Solinst Canada, Ltd. Model 615S shielded stainless steel. Temporary piezometers, designated with a "T" in the piezometer name (Table 2.1), had screen depths less than 1.2-m and generally were screened in the wetland sediment. These temporary piezometers were constructed of 0.013-m i.d. Schedule 40 PVC and were pushed into the sediment by hand. The drive points for these piezometers were also Schedule 40 PVC and had 15.2-cm long screened intervals with slot sizes of 0.00152 cm. Additional temporary piezometers were installed at 4 streambed sites, designated as "ST-" and "SWBT" (Table 2.1 and Figure 2.6). Site MW14 installed by Tetra Tech in 1998 was used as a reference point during surveying and Global Positioning System (GPS) measurements to determine locations of the "CM" piezometers. Although the relative position of all the "CM" piezometers to each other is accurate, the position of the entire "CM-" array is believed to be inaccurate because piezometers that are located on the banks of Success Branch (CM-13 and CM-14) plotted some distance from the creek channel on the areal photo (Figure 2.3). The inaccuracy may simply be due to the large scale needed for accurate positioning of the piezometers relative to the small scale of the aerial photo and the limitations of GPS. In Figures 2.5 and 2.6, the creek channel was drawn to show its correct location relative to the piezometer sites.

For the second drilling effort, a Geoprobe system mounted onto a 4x6 wheel drive all-terrain vehicle, called a John Deere "Gator," was used by Summit Drilling Co., Inc., (Bound Brook, NJ)

to collect sediment cores and install the same type of 1.9-cm inside diameter (i.d.) drive-point piezometers used in the reconnaissance effort (Figure 2.7). Difficult site access and restrictions by the New Jersey Pinelands Commission on the disturbance of wetland vegetation required unconventional drilling methods to reach greater depths and collect sediment cores. Piezometers could be installed to a maximum depth of about 17 m with the Gator, whereas the gas-powered hammer used in the reconnaissance effort could not be used to drive piezometers greater than about 4.6 to 6.1 m at this site. Although the Gator did allow installation of some deeper piezometers, its narrow ground clearance made it impossible to drive over the hummocky terrain in much of the wetland. Therefore, many sites, especially those close to the stream, could not be reached. The new site CM18 was accessed through Naval Air Engineering Station at Lakehurst and was added to help determine the extent of plume movement beneath and to the east of Success Branch.

Peepers, which are passive diffusion sampling devices that can be made in a variety of configurations (Figure 2.8), also were used to obtain ground-water samples from the shallow wetland and stream-bottom sediments along the transect to Success Branch. The high spatial resolution of shallow ground-water chemistry obtained with peepers is extremely useful in the assessment of natural attenuation in wetlands (Lorah et al., 1997; Lorah and Olsen 1999a,b). In September 2000 and March 2001, 0.61-m-long peepers were placed at sites CM3, CM9, and CM13, and 1.2-m-long peepers were placed at site ST4. The body of the peeper was constructed out of a solid 1" acrylic (Lexan) plate. There are two chambers at each depth to allow for duplicates. Two narrower sheets of acrylic are attached with screws to either side of the thick plate to hold the permeable membrane in place. The permeable membrane is a commonly used 0.2-micrometer pore size filter paper, called HT Tuffryn (Pell Corporation, Ann Arbor, MI), that is custom ordered to fit the length of the peeper. The peeper chambers are filled with deionized water that does not contain the analytes of interest before driving the peepers into the sediment by hand. While the peeper is in the subsurface, organic and inorganic components of the porewaters diffuse through the membrane into to the peeper chamber, establishing equilibrium with the porewater chemistry. A simple wooden device was used to provide leverage while removing the peepers (Figure 2.9).

### **2.2.2 Characterization of the Hydrogeology**

Continuous sediment cores were collected at Colliers Mills WMA to obtain sediment samples for descriptions of lithologic characteristics of the wetland and underlying aquifer sediments, and performance of sieve analyses to estimate hydraulic conductivities. CM18, SS1, SS2, and SS3 cores were collected at varying depths at four sites (Figure 2.2) on December 11, 2000, February 26-27, 2001, March 12, 2001, and March 13, 2001, respectively. The 9.8-m-long CM18 core was obtained at the CM18 piezometer site. The 9.8-m-long SS2 core was obtained at a location approximately 14 m south of the CM3 site and 20 m north of the CM9 site. The 1.2-m-long SS3 core was obtained at a location approximately 7.6 m southwest of the CM3 site. Attempts were made to obtain deeper core samples at these three sites, but were prevented by drill rig limitations. Sediment cores CM18, SS2 and SS3 cores were obtained using the Gator-mounted Geoprobe system (Figure 2.7). Soil cores were collected in 1.2-m-long acetate sheaths. After drilling, borehole backfill was accomplished using a mixture of Portland cement, bentonite and water, according to New Jersey Department of Environmental Protection specifications. The 122-foot SS1 core was obtained at the Lakehurst/Colliers Mills WMA boundary located near the

headwaters of Success Branch and approximately 370 m south of the A-A' transect. Access to this site was more easily accomplished and conventional drilling methods were employed. Drilling was performed by Summit Drilling Co., Inc., using a Mobil B61-HDX mud rotary drill rig. For sediment collection, 0.31-m-long, 0.05-m-diameter split spoon barrels were advanced ahead of a 0.10-m-diameter drill bit. A diluted bentonite slurry, as described above, was injected during drilling to prevent sand tunneling and borehole collapse. After completion of drilling operations, the same mixture, with an increased amount of bentonite, was used to backfill the borehole.

Potentiometric head distributions at 50 wells and temporary piezometers were determined from two sets of synoptic water-level measurements that were conducted on September 12, 2000 and March 26, 2001, prior to sampling events (Table 2.1). Water-level measurements also were made during the reconnaissance effort in November-December 1999, but some of the measurements are suspect because piezometers had just been installed and were not developed. Conventional "hold and cut" measurements were performed using chalk and stainless steel measuring tapes.

Pressure transducers were used for continuous water-level monitoring in selected piezometers at sites CM9 and CM13. Monitoring was accomplished with the use of Campbell Scientific, Inc. data loggers and Druck, Inc. pressure transducer probes. The probes were calibrated by the manufacturer within a month of their initial use in the field. Accuracy of each of the probes was  $\pm 0.007$  m.

Rising-head slug tests, using the same pressure transducers described above, were performed at various depths at the following sites: CM2-5, CM3 (upper 0.15 m of wetland sediments), CM9 (upper 0.15 m of wetland sediments), CM13-1T, CM13-2T, and CM14-5. Hydraulic conductivity results obtained from the slug tests were calculated using the Bouwer-Rice method for partially penetrating wells (Kresic, 1997):

where

$$K = \left[ \frac{r_c^2 (\ln R_e / r_w)}{2L_e} \right] \left[ \frac{1}{t} \right] \left[ \ln(s_o/s_t) \right] \quad (1)$$

$$\ln(R_e / r_w) = \frac{\left[ \frac{1}{\ln(L_w / r_w)} \right] + \left[ \frac{1/r_w}{L_e / r_w} \right]}{(2)}$$

where

- H = estimated height of water table above confining unit
- L<sub>e</sub> = length of screened interval
- L<sub>w</sub> = distance between water table and bottom of well



- $r_w = r_c$  = radial distance of undisturbed portion of aquifer from centerline = radius of the 3/4" well (i.e., no sandpack around casing)
- A = dimensionless parameter as a function of  $L_e/r_w$  plotted from Figure 31.5 from Kresic, 1997, p. 266)
- B = dimensionless parameter as a function of  $L_e/r_w$  plotted from Figure 31.5 from Kresic, 1997, p. 266)
- $(s_o/s_t)$  = displacement of hydraulic head at time zero and at time t.

Grain size distribution curves used to calculate hydraulic conductivities based on sieve analysis were determined by use of dry and wet sieving methods. Dry sieve analyses were performed on selected sediments from the CM18, SS2 and SS3 cores. A wet sieve analysis was performed on the CM13 wetland sediments because these sediments became too hardened during drying to obtain an accurate dry analysis. After wet sieving, the slurries were evaporated before size distribution weighing. Mesh sizes used for both wet and dry sieving methods were 12.70 mm, 7.93 mm, 4.75 mm, 2.00 mm, 0.85 mm, 0.425 mm, 0.25 mm, 0.149 mm, 0.075 mm, and < 0.075 mm (pan bottom). Grain size distribution curves devised by Hazen (Fetter, 1994, p. 99) were used to calculate hydraulic conductivities. Because selection of the grain size coefficient can be somewhat subjective, hydraulic conductivity values calculated by this method can result in a range of values that may vary within about half an order of magnitude. Additionally, packing of sediments based on textural maturity (roundness) can affect calculated hydraulic conductivity values. The majority of the grains in both cores were uniformly texturally immature (sub-angular).

Ground-water flow was calculated using Darcy's law (Fetter, 1994, p. 94-95):

$$Q = \frac{-KA \Delta h}{\Delta P} \quad (3)$$

where

- Q is ground-water flow ( $L^3T^{-1}$ );
- K is hydraulic conductivity ( $LT^{-1}$ );
- A is the cross-sectional area ( $L^2$ );
- $\Delta h$  is change in head along the length  $\Delta P$  (L); and
- $\Delta P$  is the length (L).

An average value of hydraulic conductivity was calculated along a flow path through the sections. Where ground-water flow was vertical, the vertical component of hydraulic conductivity also was calculated, using the equation (Lee and Fetter, 1994, p. 127-128):

$$K_z = \frac{b}{\sum (b_i/K_i)} \quad (4)$$

where

- $K_z$  is the mean vertical hydraulic conductivity ( $LT^{-1}$ );
- b is the total length of the flow line (L);

$b_i$  is the length of the  $i^{\text{th}}$  increment (L); and  
 $K_i$  is the horizontal hydraulic conductivity of the  $i^{\text{th}}$  increment ( $\text{LT}^{-1}$ ).

The specific discharge (Darcian velocity) and the average linear velocity (seepage velocity) were calculated from (Fetter, 1994, p. 145):

$$q = \frac{Q}{A} \quad (5)$$

$$v = \frac{Q}{nA} \quad (6)$$

where

$q$  is specific discharge ( $\text{LT}^{-1}$ );  
 $v$  is average linear velocity ( $\text{LT}^{-1}$ ); and  
 $n$  is effective porosity (dimensionless).

To calculate the total discharge along the sections, flow nets were constructed on a cross section that was made to scale. Flow-net analysis requires the assumptions that the aquifer is homogeneous, isotropic, and fully saturated and that the potential field does not change with time (Lee and Fetter, 1994, p. 53-60). The total discharge in a tube on the flow net is

$$Q_t = qw \quad (7)$$

where

$Q_t$  is the total discharge in flow tube per unit width of aquifer ( $\text{L}^2\text{T}^{-1}$ ); and  
 $w$  is the width of flow tube (L).

### 2.2.3 Ground-water Collection and Analysis

Ground-water samples were collected from piezometers during 3 sampling events—the November-December 1999 reconnaissance sampling, September 2000, and March 2001. During November-December 1999 when VOC analyses were made in the field, duplicate VOC samples were later analyzed using purge and trap capillary gas chromatography/mass spectrometry (GC/MS) by Baltimore USGS personnel in an on-site laboratory near the wetland site at APG, MD. The March 2001 sampling event included the 9 piezometers installed during the second drilling event. Peepers were installed and sampled in September 2000 and March 2001.

The sample collection method varied depending on the sampler type, screen depth, and the permeability of the screened material. Deeper piezometers screened in sandy aquifer sediment were purged and sampled using a peristaltic pump from which Tygon™ tubing was extended to directly above the piezometer screen. Piezometers screened in the wetland sediments, where recovery rates were generally low, were purged and sampled using a 10-mL or 60-mL syringe

attached to Teflon™ tubing that is extended to the top of the screen. Specific conductance, water temperature, and pH were monitored during purging. In piezometers with rapid water-level recovery rates, samples were collected when these parameters stabilized (agreement within 10 percent). If a piezometer became dry and did not recover within about 2 hours of removing the first casing volume of water, samples were collected immediately after water-level recovery.

Water samples for analyses of VOC's and redox-sensitive constituents (dissolved oxygen, methane, sulfide, ferrous iron, nitrate, and ammonia) generally were collected first, followed by collection of samples for other field parameters, and major ions. For collection of VOC's, two or three 8-mL vials glass vials were filled for each piezometer with a slow steady stream of water from the sampling device to minimize aeration. The vials were allowed to overflow with about three volumes of water and then immediately sealed with caps lined with a Teflon septum. Concentrations of VOCs were determined by purge and trap capillary GC/MS at the on-site laboratory trailer near the APG wetland site. The analytical method used is equivalent to USEPA Method 524.2 (Rose and Schroeder, 1995), but VOCs were analyzed on 5 ml water sample volumes instead of the more common 25 ml sample size because of the limited sample volumes obtained from the wetland sediment.

Dissolved-oxygen concentrations were measured by use of a modified Winkler colorimetric method (Baedecker and Cozzarelli, 1992) for those piezometers that contained sufficient water volume to fill a 60-mL bottle and allow it to overflow at least 2 times its volume. For many piezometers screened in the wetland sediment, dissolved oxygen was not measured because of insufficient water volumes. Sulfide was determined on unfiltered samples by a colorimetric methylene blue method, using reagents obtained in sealed ampules from CHEMetrics (Calverton, Virginia). Samples were analyzed in the field using the CHEMetrics System 1000 kit that includes a portable spectrophotometer. Nitrate and ammonia concentrations also were determined on unfiltered samples from selected piezometers using CHEMetrics System 1000 colorimetric methods. Following the method outlined by Baedecker and Cozzarelli (1992) for methane determination, unfiltered water was drawn directly from the sampling device into a 10-mL glass syringe fitted with a three-way stopcock. The methane samples were immediately transferred to sealed serum bottles that contained mercuric chloride as a preservative and that had been flushed with nitrogen gas prior to sample collection. Methane, ethane, and ethene were determined on these samples using gas chromatography with a flame ionization detector at the on-site laboratory at APG (Lorah et al., 1997). Ferrous iron was determined in samples filtered through 0.1-μm filters and immediately treated in the field with reagents specified by the colorimetric bipyridine technique (Brown et al., 1970; Baedecker and Cozzarelli, 1992). Samples were refrigerated until the absorbance was measured at the on-site laboratory on a Bausch and Lomb Spectronic 21 spectrophotometer at a wavelength of 520 nm. Samples for dissolved organic carbon (DOC) were filtered through 0.1-μm membrane filters into 12-mL glass vials and sealed with Teflon-lined septa. Samples were then analyzed at the U.S. Air Force Research Laboratory, Tyndall AFB, FL on an organic carbon analyzer. The method that was used requires acidification and sparging of the sample to remove inorganic carbon, which also removes VOC's.

Water temperature, specific conductance, and pH were measured in the field immediately after collection of unfiltered sample. Alkalinity was measured in the field immediately after collection and filtration of sample through a 0.45-micrometer (μm) membrane filter. Water temperature was measured using alcohol-filled thermometers marked in increments of 0.5 °C. Specific conductance was measured with commercial meters that were checked daily with

standard reference solutions. The pH was determined with a commercial pH meter that was equipped with a gel-filled combination pH electrode and temperature-compensation probe and calibrated with two pH buffers. Alkalinity was determined by potentiometric titration of continuously stirred samples using 0.16 N sulfuric acid to titrate to a pH of about 3.8. Alkalinity was calculated by locating the maximum of the first derivative of the curve generated from pH as a function of the titrant volume.

Water samples collected for major cations were filtered through 0.45- $\mu$ m membrane filters into polyethylene bottles and acidified immediately to pH less than 2.0 with ultrapure nitric acid. Concentrations of major cations were determined at the USGS National Water Quality Laboratory (NWQL) by inductively coupled argon plasma spectroscopy. Samples collected for major anions were filtered through 0.45- $\mu$ m membrane filters but were not treated with preservatives. Concentrations of major anions were determined by ion chromatography at the NWQL.

Peepers were filled with deionized water, placed in a water bath, and bubbled with nitrogen gas for 24 hr to remove oxygen before installing in the wetland sediment. Peepers were allowed to equilibrate with surrounding porewater for about 2 weeks before removing them to withdraw samples. A time period of 1 to 2 weeks has been determined to be sufficient for equilibration for a range of inorganic constituents and DOC (Carignan, 1984; Carignan et al., 1985). Once the peepers were removed from the sediment, the membrane was punctured and water samples were withdrawn from the chambers immediately using glass 10 mL syringes with an approximately 5.1-cm-long piece of Tygon tubing attached to the tip. Because sample sizes obtained from the peepers were very small (about 11 mL from each chamber for the 0.61-m-long peepers), only VOCs, methane, sulfide, and dissolved ferrous iron were measured. Additional constituents, including DOC and chloride, were done on samples from the 1.2-m-long peepers, which had about twice the sample volume of the 0.61-m-long peepers. These analyses were done using the same methods discussed above for the piezometers.

#### **2.2.4 Surface-water Collection and Analysis**

Surface-water samples were collected during each ground-water sampling event and analyzed for VOCs using the same method as for ground-water samples. A total of 20 surface-water samples were collected during the reconnaissance event along Elisha and Success Branch or from areas of standing water to determine areas of ground-water discharge of contaminants to surface water and thereby assist in locating the major flowpath of the contaminant plume in the wetland. A defined creek channel was not evident between surface-water sites SWB and S12 (Figure 2.6). During the later sampling events, 7 to 10 surface-water samples were collected. In addition to VOCs, selected samples were analyzed for specific conductance, dissolved oxygen, alkalinity, DOC, sulfate, and chloride using the same methods as for ground-water samples.

#### **2.2.5 Microcosm experiments**

Laboratory batch microcosm experiments were done in October-November 2000 to examine the rate of anaerobic biodegradation of TCE and 1,1,2,2-tetrachloroethane (PCA) in wetland sediment from the study site. Results of these microcosm experiments were compared to rates measured in microcosms constructed at the same time using sediment from the West Branch Canal Creek wetland site at APG and to previous microcosm experiments with APG wetland sediment (Lorah et al., 1997). Although PCA was not a contaminant at the Colliers Mills WMA

site, PCA was included because it is a major contaminant at the APG wetland site. Microcosms were constructed under methanogenic conditions using the same preparation and incubation methods reported previously (Lorah et al., 1997; Lorah and Olsen, 1999a). For the Colliers Mills WMA microcosms, wetland sediment was collected from a depth of 0 to 25.4 cm near site CM13. Porewater was collected from nearby piezometer CM14-5 (Figure 2.6). This piezometer was used because it can be pumped without drawdown. All microcosms were constructed under a nitrogen atmosphere in 162-mL serum bottles using a 1.5:1 volumetric ratio of ground water to wetland sediment and incubated upside down in the dark at 19 °C. Microcosms were amended with 1,200 µg/L of TCE (9.12 µmol/L) or PCA (7.15 µmol/L) at day 0. Duplicate microcosm bottles were prepared for each treatment and sacrificed for analyses of VOCs, ferrous iron, sulfate, and methane in the microcosm water at each time step. Experiments also included sterile controls that were prepared with 1 percent by volume of formaldehyde for each treatment, and water controls that did not contain any sediment and were amended with TCE and PCA.

### **2.2.6 Characterization of Sorption and Phytoremediation**

Sorption and phytoremediation are two potentially significant natural attenuation processes in the wetland sediments that were evaluated at the Colliers Mills WMA wetland site. VOC analyses of wetland sediment samples were done to give a direct indication of the importance of sorption. Selected sediment samples collected during drilling in December 2000-March 2001 were analyzed for VOCs. Duplicate sediment samples (10 g) for each depth were placed in pre-weighed 40-mL VOC vials containing 20 mL of methanol, and the methanol extraction was analyzed by GC/MS using EPA Method 5035 at the USGS laboratory trailer at APG. To determine dry weight percent of the sediment samples, a third 40-mL VOC vial that did not contain methanol was filled with 10 g of sediment.

Phytoremediation (the uptake, translocation and possible transformation of ground-water contaminants by vascular plants) is presently an evolving field with no standard procedures for assessment. The uptake of TCE and other VOCs by trees, particularly the cedars that are abundant at the site, were examined using the tree coring and chemical analysis procedure of Vroblesky et al. (1999). In addition to using the method reported by Vroblesky et al. (1999) of putting tree cores in an empty 40 mL VOC vial and analyzing the headspace, a duplicate tree core sample for each tree was placed in methanol in the VOC vial and the methanol extract was analyzed. The methanol extract analyses are reported here because these gave the most consistent and highest detections of VOCs. The potential for uptake by plants also was evaluated using the continuous water-level data obtained at sites CM9 and CM13 to determine potential diurnal changes caused by plant uptake of ground water.

### **2.3 Evidence of Natural Attenuation in a Forested Swamp (Colliers Mills Wildlife Management Area, New Jersey)**

Site characterization needed to assess natural attenuation processes include (1) definition of a major ground-water flowpath and characterization of local geology and ground-water flow; (2) determination of concentrations of parent contaminants, daughter product concentrations, and redox-sensitive constituents to assess biodegradation processes; and 4) assessment of the

occurrence of other possible significant attenuation processes (Wiedemeier et al., 1998). Laboratory microcosm experiments assist in identifying biodegradation reactions and controlling factors and in quantifying biodegradation rates (Wiedemeier et al., 1998; Lorah et al., in press). Detailed assessment of site hydrogeology and geochemistry over small vertical scales is particularly crucial in a wetland system because it is a ground-water discharge zone and a ground-water/surface water interface region. The shallow flow system and connection with surface water can also cause seasonal greater fluctuations in natural attenuation processes in wetlands than those observed in deeper aquifers (Lorah et al., in press). Because of logistical constraints in this study, complete ground-water flow and geochemical data were obtained only during two seasons—the dry season (September 2000) and the wet season (March 2001). Although the reconnaissance event in November-December 1999 established the major ground-water flowpath of the contaminants through the wetland area, evaluation of natural attenuation processes was incomplete during this sampling event. The effects of well recovery after installation and development of the piezometers caused water-level measurements to be suspect and limited the constituents analyzed in some piezometers. In addition, characterization of the geochemistry of the wetland porewater was limited because piezometers were not installed during this reconnaissance event. The September 2000 and March 2001 sampling data, combined with the microcosm results, allow a fairly detailed evaluation of natural attenuation processes in the wetland, but additional seasonal characterization would be desirable to fully evaluate the feasibility of monitored natural attenuation as a ground-water remediation method for the TCE plume at this site. The results of the natural attenuation evaluation in the Colliers Mills WMA wetland site are discussed below; hydrogeologic and geochemical data that were collected are given in Appendix C.

### **2.3.1 Characterization of the Hydrogeology**

#### **2.3.1.1 Lithology and Mineralogy**

The geology in the wetland study area consists of a 0.30- to 1.2-m thick layer of organic-rich peat and silty to sandy clays, overlying a seaward-dipping wedge of unconsolidated sediments of the Kirkwood-Cohansey aquifer system (Figure 2.10). Detailed lithologic descriptions prepared from three cores taken within the study area can be found in Appendix C. The sediments generally strike northeast-southwest and dip gently to the southeast 1.9 to 11 m/km (Zapecza, 1989). A 37-m core (SS1) taken at the site revealed that the Cohansey Sand of Miocene age is approximately 21-m thick and overlies the 15-m thick Kirkwood Formation, also of Miocene age (Figure 2.10). Lying within the lower portion of the Kirkwood Formation is the Alloway Clay Member. This 12- to 18-m thick confining clay unit forms the basal surface for the Kirkwood-Cohansey aquifer (Zapecza, 1989). The Miocene beds were deposited in various shelf and beach environments created by alternating transgressive (Alloway Clay) and regressive (upper Kirkwood and Cohansey) seas, and underlie an area of about 3000 mi<sup>2</sup> in central and southern New Jersey (Zapecza, 1989).

The Cohansey Sand in the study area consists of light-colored, fine- to coarse-grained quartz sand that contains occasional pebbly, silty and clayey sands, and several very thin interbedded silty-clay layers or lenses. The extent and positions of these thin lenses are variable throughout the study site. Red to orange to yellow iron staining is common throughout the sand and gravel within this geologic unit. The Cohansey Sand contains secondary kaolinite, gibbsite and silica;



only small amounts of potassium and sodium feldspars; and virtually no other weatherable silicate minerals (Owens and Sohl, 1969). At the BOMARC site upgradient of the wetland, Tetra Tech (1999) observed a 0.61- to 3.0-m thick organic silt and peat strata lying between two distinct sand layers-- an upper 7.6- to 15-m thick strata of tan to orange coarse to fine sand and an underlying 3.0- to 11-m thick strata of dark gray to brown fine sand with minor amounts of silt. This silt/peat layer was not observed in the sediment cores taken from the Colliers Mills site.

The Kirkwood Formation is hydraulically connected to the Cohansey Sand but is much finer grained than the Cohansey Sand. The Kirkwood Formation consists of light- to medium-grey, fine- to medium-grained silty sands. Although not seen in any of the cores taken from the study area, Zapecza (1989) states that some local clay beds within the Cohansey Sand are relatively thick, and that perched water tables and semi-confined conditions can exist locally within the Kirkwood Formation. The basal confining Alloway Clay Member of the Kirkwood Formation is a tight, greenish-grey, glauconitic clay.

#### **2.3.1.2 Flow Directions and Head Distributions**

Head distributions and flow directions along section A-A' in the Colliers Mills WMA are shown in Figure 2.11 for synoptic measurements on September 12, 2000 and March 27, 2001. The September 2000 synoptic water-level data show that the principal ground-water flow direction in the Colliers Mills WMA was northeastward toward Success Branch, as was indicated by earlier water-level measurements upgradient of the wetland study area (Tetra Tech, 1999). In the upland area near site CM17 in September 2000, flow directions at shallow to moderate depths in the aquifer were downward, indicating recharge (Figure 2.11a). Moving northeastward into the wetland area, the head gradient changed near site CM16 to indicate upward ground-water flow. Vertically upward flow predominated in the area from site CM16 to CM14 (Figure 2.11a), showing that ground-water discharge occurred in September 2000 once the wetland sediments were encountered. There were flow anomalies at site CM9, however, as shown by the head gradient reversals at alternating depths in the shallow wells (Figure 2.11a). A low hydraulic conductivity lens in the vicinity of the CM9-5 well depth could cause refraction of the flow direction. A clogged well screen also could produce apparent flow direction changes. A slug test was attempted at CM9-5 but was aborted because equilibrium was not attained within an acceptable time period.

A limited number of wells were installed at depths greater than 6.1 m into the Kirkwood-Cohansey aquifer system. Flow deep in the aquifer within Colliers Mills WMA is presumed to be laterally northeastward and then upward toward Elisha and Success Branches. It is not known at what depths ground water movement becomes unaffected by Elisha and Success Branches and bypasses them, with movement directed laterally beneath the creeks. The sections in Figure 2.11 represent 2-dimensional flow, and do not depict possible downstream flow in Success Branch. This third dimension appears under the stream as "dead space" and represents a component of flow downstream (into the paper).

Compared to the September 2000 synoptic data, the March 2001 synoptic water-level measurements show that there was a reversal in flow direction within most of the wetland area



(Figures 2.11a,b). Shallow flow in the wetland area was directed predominantly downward in March 2001 with recharge evident at shallow depths between sites CM9 and CM12 (Figure 2.11b). Between CM12 and CM13, however, a hinge line [a line that separates the recharge and discharge areas (Freeze and Cherry, 1979)] existed where the ground water changed direction to discharge directly into Success Branch. At moderate depths through much of the wetland, however, upward flow was still occurring. The change in flow regimes between the two dates may be attributed to the differences between a dry fall and a spring flush. With the exception of 2.54 cm of precipitation that occurred a week prior to the September 2000 synoptic measurements, only 0.74 cm additional rain fell in the 30 days before the synoptic measurements were taken. In contrast, 10.9 cm of rain were recorded during the 30 days prior to the March 2001 synoptic measurements. Additionally, a warming trend in mid-March created a snowmelt (93.7 cm of snow fell from December 2000 to early March 2001) that contributed significantly to the ground-water influx.

Hydrographs were constructed from continuous water-level measurements in CM9-3T, CM9-10.5, CM13-2T, CM13-12, and CM13-21 for approximately 10 months in 2001 (Figure 2.12). These hydrographs show responses of water levels to precipitation events and illustrate changes in head distributions and ground-water flow directions over time. At site CM9, potentiometric head elevations in the 3.2-m-deep piezometer always remained higher than those of the 0.91-m-deep piezometer, indicating a constant upward head gradient toward the wetland sediments (Figure 2.12a). However, after a long dry spell (from mid-April through mid-May 2001), the water level in the 3.2-m-deep piezometer decreased more rapidly than the water level in the 0.91-m-deep piezometer, so that the heads in the two wells became approximately equal (Figure 2.12a). Although an upward flow component remained after May 2001, the principal ground-water-flow direction was horizontal. After June 15 (and the long dry spell), precipitation events greater than 2.54 cm caused very high spikes in the water levels, but the lack of frequent smaller events in the interims allowed the base water levels in both piezometers to decline rapidly. Close inspection of hydrographs for short time periods around these spikes showed little difference (less than 3 hr) between the two piezometers in the lag time to respond to these precipitation events. The similar response of the two piezometers indicates that they are hydrologically connected. If a clay lens is present at a depth of approximately 1.5 m as suggested by flow anomalies in the synoptic head distributions (Figure 2.11a), the lens could not be extensive.

At site CM13, there were larger differences in the water-level elevations between the shallow 0.61-m-deep piezometer and the two deeper piezometers (CM13-12 and CM13-21) than there were between the 0.61-m- and 3.2-m-deep piezometers at CM9. Therefore, a stronger vertical gradient was evident at site CM13, which is adjacent to Success Branch, than at site CM9, which is near the wetland/upland boundary. Hydraulic heads always remained lower in the 0.61 m piezometer than the deeper wells, indicating that at shallow depths near the stream there was continuous discharge. The potentiometric heads at the 3.6-m-deep piezometer at site CM13 were similar to those in the 6.4-m-deep piezometer during January to mid-March, indicating that the flow direction was predominantly horizontal deeper in the aquifer during this time. During and after the spring flush in mid-March, the ground-water-flow direction changed to predominantly vertically upward in the 3.6- to 6.4-m depth range. At all times of the year, however, brief periods of gradient reversals occurred during and after high precipitation events, so that vertically downward flow from CM13-12 (3.6 m deep) to CM13-21 (6.4 m deep) was predominant for short periods. In addition, vertically downward flow from CM13-12 (3.6 m deep) to CM13-21 (6.4 m deep) was predominant during late June to late July because water

levels declined faster in CM13-21 after high precipitation events (Figure 2.12b). After another fairly dry period, upward flow again predominated. After a precipitation event, the water levels in the 0.61-m- and 3.6-m-deep piezometers peaked at the same time, whereas the 6.4-m-deep piezometer peaked an average of 18 hr later. This large lag time between the 6.4-m-deep piezometer and the shallower piezometers indicates that there may not be a direct hydrological connection in the 3.6 to 6.4 m depth range. Water levels peaked at CM13-2T (0.61 m deep) and CM13-12 (3.6 m deep) at nearly the same time water levels peaked at CM9-3T (0.91 m deep) and CM9-10.5 (3.2 m deep) during precipitation events. Thus, all monitored wells except CM13-21 (6.4 m deep) responded rapidly to the influx of water.

### 2.3.1.3 Hydraulic Conductivities

Two methods were used to estimate hydraulic conductivity values at the Colliers Mills Site. Data were collected from slug tests that were conducted between February and August 2001. Additionally, sieve analyses were performed on sediments from cores at selected depth intervals. The sediments were obtained from continuous cores collected at sites near CM18 (CM18 Core) and CM3 (SS2 and SS3 Cores) (Figure 2.10). Adequate samples of the upper 0.61 m of wetland sediments were difficult to obtain during coring because the shallow sediments were greatly compressed or lost during drilling operations due to the presence of tree roots. Therefore, wetland sediment samples for sieve analysis were obtained at site CM13 by manual digging; these samples represent wetland sediments near Success Branch at depths between approximately 0.076 and 0.30 m below land surface.

Horizontal hydraulic conductivities calculated from slug tests and sieve analysis for aquifer and wetland sediments at the Colliers Mills site are presented in Tables 2.2 and 2.3. Horizontal hydraulic conductivity is about an order of magnitude greater in the aquifer sediments than the wetland sediments. The median of 41 values estimated for the aquifer sediments is 27.7 m/day, with a range of 5.5 to 140 m/day. The estimated hydraulic conductivities for the Kirkwood-Cohansey Aquifer are typical of an aquifer composed of fine to coarse sands (Domenico and Schwartz, 1990, Table 3.2), with lenses of both coarse, gravelly material and finer sands and silts. The median of 5 values estimated for the wetland sediments is 1.8 m/day, with a range of 0.46 to 10 m/day (Tables 2.2 and 2.3).

These estimates of horizontal hydraulic conductivity at the Colliers Mills WMA compare well to results from previous studies conducted in the upper Kirkwood-Cohansey aquifer system in central and southern New Jersey. Gill (1962) and Rhodehamel (1973) measured horizontal hydraulic conductivities of 27 to 76 m/day in aquifer tests in the upper Kirkwood-Cohansey aquifer system in New Jersey. Martin (1998) estimated horizontal hydraulic conductivities estimates ranging from 15 to 98 m/day based on specific-capacity tests and estimates of transmissivity. Within the lower Kirkwood-Cohansey aquifer system, Gill (1962) reported horizontal hydraulic conductivity values of 12 to 46 m/day, and Martin (1998) estimated values of 10 to 98 m/day.

**Table 2.2. Horizontal hydraulic conductivities (K) from sieve analyses of aquifer and wetland sediments in the Colliers Mills study area, New Jersey.**

Sediment site	Depth (m)	Lithologic Unit	K (ft/day)	K (m/day)
CM13 (grab)	0.15 – 0.46	wetland sediments	1.5	0.46
SS2	.58-.67	aquifer	82	25
SS2	.79-.83	aquifer	460	140
SS2	.85-.88	aquifer	160	49
SS2	.91-.94	aquifer	120	37
SS2	.97-1.0	aquifer	130	40
SS2	1.0-1.1	aquifer	140	43
SS2	1.4-1.6	aquifer	120	37
SS2	1.6-1.8	aquifer	130	40
SS2	2.8-3.0	aquifer	48	15
SS2	3.0-3.1	aquifer	57	17
SS2	3.1-3.3	aquifer	42	13
SS2	3.3-3.6	aquifer	64	20
SS2	4.0-4.3	aquifer	180	55
SS2	4.7-4.8	aquifer	170	52
SS2	5.0-5.3	aquifer	130	40
SS2	5.9-6.0	aquifer	26	7.9
SS2	6.5-6.7	aquifer	18	5.5
SS2	8.0-8.1	aquifer	13	4.0
SS2	9.2-9.3	aquifer	65	20
SS2	9.3-9.4	aquifer	91	28
SS3	.82-1.2	aquifer	120	36
SS3	.82-1.2	aquifer	280	85
CM18	.18-.61	aquifer	82	25
CM18	.73-1.0	aquifer	56	17
CM18	1.0-1.2	aquifer	73	22
CM18	1.9-2.4	aquifer	102	30
CM18	2.4-2.7	aquifer	73	22
CM18	3.4-3.6	aquifer	73	22
CM18	3.6-4.0	aquifer	192	58
CM18	4.7-4.9	aquifer	82	25
CM18	4.9-5.2	aquifer	92	28
CM18	5.8-6.1	aquifer	64	20
CM18	6.1-6.6	aquifer	64	20
CM18	7.0-7.3	aquifer	56	17
CM18	7.3-7.5	aquifer	125	38
CM18	8.5-9.0	aquifer	160	49
CM18	9.0-9.2	aquifer	160	49
CM18	9.0-9.2	aquifer	160	49
CM18	9.2-9.7	aquifer	110	34

**Table 2.3. Horizontal hydraulic conductivities measured by slug tests in piezometers in the Colliers Mills WMA wetland study area, New Jersey.**

Sediment site	Depth (m)	Lithologic unit	K (ft/day)	K (m/day)
CM2-5 <sup>a</sup>	1.4 – 1.5	aquifer	1.5	0.46
CM9-5 <sup>b</sup>	1.5 – 1.7	aquifer	82	25
CM12-12 <sup>b</sup>	3.5 – 3.7	aquifer	460	140
CM14-5 <sup>c</sup>	1.4 – 1.5	aquifer	160	49
CM3 <sup>d</sup>	0 - .15	wetland sediments	120	37
CM9 <sup>d</sup>	0 -.15	wetland sediments	130	40
CM13-1T <sup>e</sup>	.15 - .31	wetland sediments	140	43
CM13-2T <sup>f</sup>	.46 - .61	wetland sediments	120	37
CM2-5 <sup>a</sup>	1.4 – 1.5	aquifer	130	40

<sup>a</sup>Average of 7 slug tests.

<sup>b</sup>Screened interval may be in low conductivity lens.

<sup>c</sup>Average of 5 slug tests.

<sup>d</sup>Average of 4 slug tests performed with a 13-cm-diameter slotted stainless-steel drive-point piezometer.

<sup>e</sup>Average of 5 slug tests.

<sup>f</sup>Average of 4 slug tests.

Because the flow between CM16 and Success Branch is vertical (Figure 2.11), the effective vertical hydraulic conductivity ( $K_z$ ) was estimated using Equation 4 and the harmonic mean of the horizontal hydraulic conductivity estimates from the 9.8-m-long SS2 (Figure 2.10). The core length was divided into 22 increments with  $b_i$  varying from 0.003 to 0.46 m and  $K_i$  varying from 0.00015 to 140 m/day. From these calculations, the average  $K_z$  was estimated to be 0.144 m/day. Although this  $K_z$  cannot be assumed to be the same throughout the entire wetland area, this value provides a general estimate of vertical hydraulic conductivity for use in discharge and velocity calculations. Martin (1998) estimated  $K_z$  of the Kirkwood-Cohansey aquifer system in ground-water-flow simulations to be 0.01 times the aquifers' horizontal hydraulic conductivity, giving values of 0.10 to 0.98 m/day.

#### 2.3.1.4 Discharge Rates and Flow Velocities

The specific discharge of ground water to the wetland surface and the average linear flow velocities through the aquifer and wetland sediments were estimated from the September 2000 synoptic measurements along cross-section A-A', beginning at the hinge line near CM16 and continuing northeast to Success Branch (Figure 2.11a). Using Equations 3 and 5 for the flow line B-B' near site CM9 (Figure 2.11a), the specific discharge,  $q$ , at the wetland surface was calculated to be 0.0013 m/day for a unit area of 1 m<sup>2</sup>. Specific discharge values for all flow lines ranged from 0.00085 to 0.0016 m/day per unit aquifer width, with a mean value of 0.0013 m/day per unit aquifer width. This is equivalent to 46.5 cm/yr.

To estimate total discharge per unit width of aquifer ( $Q$ , Equation 7), a flow net also was constructed along cross-section A-A' for the same date (on file, USGS, Baltimore, MD). A flow net that contained 54 flow tubes was constructed along a transect in the wetland between the hinge line near CM16 and Success Branch. As an example, the center flow-stream line of flow tube 44 is shown in Figure 2.11a as B-B', the same flow line that was used in the previous calculations. The length of this flow tube is 11.6 m and the change in head is 0.107 m. Substituting  $K_z$  and these values into Equations 7 and 8, discharge is 0.0044 m<sup>2</sup>/day for this particular flow tube. These calculations were performed on all 54 flow tubes, each of which had varying lengths and head differences. Summing all discharge values from the flow net calculations, the total discharge along a 1-m-wide strip of the wetland surface is 0.25 m<sup>2</sup>/day. If the specific discharge value calculated in the previous paragraph is converted to total discharge (Equation 7), the previous method results in a value of 0.313 m<sup>2</sup>/d. The two estimates of total discharge agree within the range of uncertainties that exist for all the variables in both methods.

To calculate the average linear velocity ( $v$ ) for the aquifer along the flow line B-B', an estimated effective porosity of 0.3 was used, which is typical of fine to coarse sands with interfingers of clay and gravel (Fetter, 1994). Substituting the porosity factor of 0.3 and the mean specific discharge value ( $q$ ) of 0.0013 m/d into Equation 6, the average linear velocity is about 0.0043 m/day or 1.6 m/yr. This estimated value is based on the assumption that thin clay or fine silt layers are intermittently present throughout the aquifer. In areas where the lower conductivity layers are breached or not present, the flow velocities in the aquifer could be more than an order of magnitude higher than 1.6 m/yr.

The average linear velocities of ground water through the wetland sediments may vary significantly depending on location within the Colliers Mills WMA. The wetland sediments are composed of varying amounts of clay, peat and sand. The thickness of this layer was also found

to vary greatly by site location. The horizontal hydraulic conductivity measured on the grab samples of wetland sediments near site CM13 was estimated to be about 0.46 m/day (Table 2.2). If vertical hydraulic conductivity is estimated to be about 0.01 times the horizontal hydraulic conductivity (Martin, 1998), the vertical hydraulic conductivity for these sediments is approximately 0.0046 m/day. Assuming an effective porosity of 0.4 [typical of silts and clays with less than 35 percent organic carbon (Mitsch and Gosselink, 1986; Fetter, 1994)], the average linear velocity from Equation 6 is 0.00034 m/day (0.12 m/yr), which is an order of magnitude lower than the estimated linear velocity in the aquifer. However, the presence of tree roots, peat, and coarse sand and gravel throughout the wetland sediments most likely produces much higher flow velocities than estimated from the vertical hydraulic conductivity and porosity. The actual linear velocities in the wetland sediments may be only slightly lower than the velocity in the aquifer at many locations.

At greater depths in the aquifer, the ground-water flow in the aquifer could be predominantly horizontal and unaffected by Success Branch and the overlying lower-conductivity wetland sediments. Average linear velocities for purely horizontal flow in the aquifer were estimated using (1) median horizontal hydraulic conductivity values from the sieve analyses (28 m/day) and the head gradient from the hinge line near the CM16 site to the CM13 site (Figure 2.11a), and (2) median horizontal hydraulic conductivity values from slug tests (13.6 m/day) (Table 2.3) and the head gradient at sites CM2-5 and CM14-5 (Figure 2.11a). Assuming an effective porosity of 0.3, the average linear velocity is 0.314 m/day (115 m/yr) based on the sieve analyses and 0.140 m/day (51.2 m/yr) based on the slug tests. These results compare well with the Tetra Tech (1999) study that showed flow velocities between 0.10 and 0.22 m/day (36.5-80.3 m/yr) at the BOMARC Missile Site.

### **2.3.2 Ground-Water and Surface-Water Chemistry and Evidence of Biodegradation**

#### **2.3.2.1 Reconnaissance Phase Sampling (November-December 1999)**

During the reconnaissance piezometer installation and sampling event, TCE and cisDCE were the only VOCs detected in the aquifer and wetland porewater (Appendix C; Figure 2.5). VC, ethene, and ethane were not detected. TCE concentrations in the aquifer were highest near the wetland boundary at sites CM16 and CM17 and at the greatest depths sampled in the aquifer (screen depths of 8.5 m and 7.0 m, sites CM16 and CM17 in Figure 2.5). TCE concentrations at depths of 8.5 m and 7.0 m, respectively, were 490 and 430  $\mu\text{g/L}$  at sites CM16 and CM17 (Figure 2.5). Previous investigations (TetraTech, 1999) showed TCE concentrations of 190 and 420  $\mu\text{g/L}$  at depths of about 14 m in samples from nearby upland monitoring wells MW10 and MW14 (Figure 2.5). Although the TCE plume seems to extend to great depths in the aquifer, drive-point piezometers could not be installed greater than 8.5 m in the wetland study area with the electric hammer used during this reconnaissance event. At the upland site CM17, TCE concentration was only 2.6  $\mu\text{g/L}$  at a depth of 3.6 m in the aquifer. The lower TCE concentration at shallow depths in the aquifer indicate that ground water is not discharging upward at this site, which was supported by the downward head gradients at this site during two synoptic water-level measurements (Figure 2.11). At shallow depths in the aquifer (3.6 m or less) along the wetland boundary, TCE concentrations were highest at CM3, with 110 and 220  $\mu\text{g/L}$  detected in 2.4-m- and 3.6-m-deep piezometers, respectively (Figure 2.5). Therefore, nested drive-point piezometers were installed from the wetland boundary near CM3 to Success Branch along the



general northeastward direction of flow in the aquifer. At site CM13 adjacent to the west bank of the stream, TCE concentrations were about 200 µg/L at depths of 3.6 m and 6.4 m, indicating upward flow of the contaminant in the aquifer (Figure 2.5).

The highest concentrations of cisDCE in the aquifer during this reconnaissance event were about 20 µg/L, which is an order of magnitude lower than the highest TCE concentrations in the aquifer (Figure 2.5). The low cisDCE concentrations and undetectable VC and ethene concentrations indicate that little reductive dechlorination of TCE was occurring in the aquifer. Although not all redox constituents were analyzed in all samples in the reconnaissance event, the relatively high dissolved-oxygen concentrations in the aquifer (0.89 to 7.24 mg/L) indicated aerobic conditions. Little reductive dechlorination of TCE would be expected under these conditions.

In samples collected from piezometers screened in the wetland sediment during the reconnaissance event, TCE concentrations were highest at CM13 adjacent to Success Branch (Figure 2.6). TCE concentrations were 130 and 150 µg/L, respectively, at depths of 0.30 and 0.61 m at CM13. Except for site CM9, TCE and cisDCE concentrations were less than 20 µg/L in the wetland porewater sampled with the piezometers (Figure 2.6). Little upward discharge of contaminants to the wetland sediments, therefore, seems to occur until the stream is reached. Compared to other wetland porewater piezometers, site CM9 had anomalously high cDCE concentration of 130 µg/L at a depth of 0.91 m below land surface (Figure 2.6). Piezometers screened at shallow depths (0.30 to 1.2 m) in the streambed near site CM13 had TCE concentrations ranging from 110 to 250 µg/L and cisDCE concentrations ranging from 2.3 to 48 µg/L (sites ST1, ST2, ST3 in Figure 2.6). Thus, relatively low concentrations of cisDCE were observed in the shallow piezometers (0.30 to 1.2 m depth) except at site CM9. The low concentrations of TCE daughter products measured in piezometers during the reconnaissance sampling suggested that little degradation was occurring in the wetland sediments. The wetland sediments are thin, however, and many of these piezometers are screened at top of the aquifer or near the interface of the aquifer and wetland sediments. The greater vertical resolution from the peepers used in the September 2000 and March 2001 sampling events is needed to evaluate biodegradation in the wetland sediments. In addition, because of slow recoveries after installation and purging, redox constituents were not measured in many of the piezometers installed in the wetland sediment during this reconnaissance event to evaluate the presence or absence of conditions appropriate for anaerobic degradation.

#### **2.3.2.2 Piezometer Sampling in September 2000 and March 2001**

Except for the addition of streambed piezometers at sites ST4, ST5, and ST6, the piezometers sampled in September 2000 were the same as those in the reconnaissance phase sampling (Figures 2.5, 2.6, 2.13, and 2.14). In March 2001, additional deep piezometers were added at sites CM3, CM4, CM9, CM17, and a new site was added at CM18 to the east of the creek (Figures 2.13 and 2.14). All piezometers were sampled for a more comprehensive list of constituents in September 2000 and March 2001 than previously obtained (Appendix C).

As observed in November-December 1999, the major VOCs detected in the piezometer samples during September 2000 and March 2001 were TCE and cisDCE. VC was detected only in CM9-1T and CM9-3T and at a low concentration (1.0 µg/L) (Appendix C). Ethene or ethane was not detected in any samples (data not shown). Figures 12.13 and 12.14 show VOC concentrations measured in the aquifer and wetland sediment from piezometer samples collected



in September 2000, with data for the new wells added. Piezometer samples collected during September 2000 had similar concentrations of VOCs as those collected during the reconnaissance phase (November-December 1999), except that a few samples had higher concentrations in this second sampling round. For example, TCE concentrations were 360  $\mu\text{g/L}$  in CM9-21 and CM13-21 in September 2000 (Figure 12.13), whereas concentrations were 76 and 220  $\mu\text{g/L}$ , respectively, in these piezometers in November-December 1999 (Figure 2.5). The higher VOC concentrations in September 2000 may be due to better well development and recovery than when sampling was done immediately after the reconnaissance drilling. The highest TCE concentration detected in the aquifer was in the new deep well at site CM9, screened at a depth of 10 m below land surface (Figure 2.13). Along the transect from site CM9 to the stream by CM13, TCE concentrations in the aquifer were highest in the deepest piezometer at each site, except site CM13 (Figure 2.15). The more uniform concentrations in the aquifer at site CM13 indicate strong upward flow with little TCE degradation occurring in the aquifer.

In the shallow ground water in the wetland, the highest TCE concentrations were observed at piezometer site CM-13 adjacent to the west bank of Success Branch, again indicating strong upward discharge from the aquifer. For the streambed piezometers, samples at sites ST1 and ST2, which are immediately upstream and downstream of site CM13, showed the highest TCE concentrations (Figure 2.14 and 2.16). TCE concentrations were between about 200 and 400  $\mu\text{g/L}$  at a depth of 0.30 to 0.91 m below land surface at these sites (Figure 2.16). During the 3 sampling events, TCE concentrations in the surface water consistently were highest in the approximately 110-m-long reach between sites S9 and S15 (Figure 2.17), which corresponds to streambed piezometer sites ST2 to a little downstream of ST1 (Figure 2.14). Thus, the combined piezometer and surface-water data indicate that the TCE plume predominantly discharges in a relatively narrow area with the center near site CM13.

Because the TCE plume appears to remain relatively deep in the aquifer until close to the stream, the TCE plume most likely was missed by some of the piezometer nests along the wetland boundary that had screens at a maximum depth of 3.6 m (Figure 2.13). The 10-m-deep piezometer newly added at site CM4 in 2001 had a TCE concentration of 57.9  $\mu\text{g/L}$ , whereas the 3.6-m- and 5.2-m-deep piezometers at this site had concentrations of 0.7 and less than 0.5  $\mu\text{g/L}$ , respectively (Figure 2.13). The streambed piezometers and surface-water samples, however, assist in defining the areal extent of the TCE plume. From the existing piezometer network, the extent of TCE transport beneath and east of the creek is unclear. Samples from the aquifer at site CM14 had 11  $\mu\text{g/L}$  TCE during one sampling event (Figure 2.5), and samples from the deepest piezometer (17 m) at CM18 (east of CM14) had a TCE concentration of 1.58  $\mu\text{g/L}$  (figure 2.14). Although these concentrations are low, they may indicate some eastward movement of the plume beneath the creek.

Comparison of TCE and cisDCE concentrations indicates that little anaerobic degradation of TCE is occurring in the aquifer. Reductive dechlorination of TCE would produce equimolar concentrations of cisDCE. A plot of cisDCE compared to TCE concentrations in the piezometer samples show a low ratio of cisDCE:TCE in all samples from the aquifer, indicating that little reductive dechlorination has occurred (Figure 2.18a). Measurement of the concentrations of redox-sensitive constituents in the aquifer did not give a clear indication of the potential for reductive dechlorination to occur (Table 2.4). The mean dissolved oxygen concentrations in the aquifer was 2.98 and 3.72 mg/L on September 2000 and March 2001, respectively, showing generally aerobic conditions and little potential for reductive dechlorination. Methane and

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ferrous iron also were frequently detected in the aquifer, however, indicating that anaerobic microzones may exist where reductive dechlorination could occur (Table 2.4).

**Table 2.4.** Descriptive statistics for selected inorganic and organic constituents measured in samples from piezometers and surface water during September 2000 and March 2001, Colliers Mills WMA wetland site aquifer.

[Statistics were done using only piezometers that were sampled on both sampling trips and using only detected values. Therefore, "count" is the number of detections. pH is in standard units; Cond.= specific conductance in microsiemens per centimeter; DO= dissolved oxygen in milligrams per liter (mg/L); Fe<sup>2+</sup> = ferrous iron in mg/L; DOC = dissolved organic carbon in mg/L; sulfate, chloride, and sulfide are also in mg/L; methane is in micrograms per liter; TCE and cisDCE= trichloroethene and 1,2-*cis*-dichloroethene in micrograms per liter.]

Constituent	Mean	Median	Min.	Max.	No. of samples	Mean	Median	Min.	Max.	No. of samples
<i>September 2000- Aquifer</i>						<i>September 2000- Wetland Porewater</i>				
pH	5.38	5.36	4.39	6.10	33	4.78	4.84	4.08	5.45	12
Cond.	70	66	30	146	34	56	53	30	91	12
DO	2.98	2.21	0	7.43	27	--	--	--	--	--
Sulfate	10.5	8.28	2.84	41.2	31	7.38	7.12	1.91	17.2	11
Chloride	2.81	2.44	1.80	6.39	31	3.72	3.49	2.40	7.44	11
Fe <sup>2+</sup>	4.65	3.84	0.04	12.2	27	2.78	0.18	0.07	9.98	9
Sulfide	--	--	--	--	--	0.28	0.14	0.01	1.15	10
Methane	554	360	68	1850	20	834	419	56	3440	8
DOC	7.4	5.0	1.0	28	33	17.2	5.2	1.0	57	10
TCE	173	73.0	0.6	570	26	48.7	50.4	0.7	244	16
cisDCE	10.0	7.6	0.9	42.8	21	43.4	10.0	0.5	226	8
<i>March 2001-- Aquifer</i>						<i>March 2001-- Wetland Porewater</i>				
pH	5.46	5.51	4.62	6.38	33	4.77	4.80	4.14	5.52	10
Cond.	73	76	11	129	33	64	58	44	106	8
DO	3.72	2.80	0.4	7.60	28	--	--	--	--	--
Sulfate	16.1	13.8	1.61	46.0	28	12.7	13.7	1.79	21.5	11
Chloride	3.26	2.92	1.85	6.80	28	3.39	3.51	2.30	4.28	11
Fe <sup>2+</sup>	3.12	2.52	0.01	10.7	32	1.63	0.75	0.02	7.51	11
Sulfide	--	--	--	--	--	0.19	0.06	0.01	1.04	7
Methane	367	179	40	1800	22	310	86	52	837	6
DOC	9.4	8.0	2.0	22	27	18.5	9.5	3.0	95	14
TCE	180	165	0.6	611	24	82.0	4.28	0.73	391	12
cisDCE	9.46	6.34	1.04	43.2	21	48.2	8.30	1.05	172	9
<i>September 2000- Surface Water</i>										
Cond.	57	56	54	63	6	--	--	--	--	--
DO	3.38	3.40	2.87	4.04	5	--	--	--	--	--
TCE	18.5	20.4	9.8	22	5	--	--	--	--	--
cisDCE	0.88	0.85	0.80	1.0	4	--	--	--	--	--
<i>March 2001--Surface Water</i>										
Cond.	53	52	46	64	6	--	--	--	--	--
DO	6.86	7.00	6.20	7.30	5	--	--	--	--	--
TCE	22.9	17.1	0.84	68.1	6	--	--	--	--	--
cisDCE	0.82	0.48	0.46	1.9	4	--	--	--	--	--

Alternatively, the methane detected in the aquifer could have resulted from downward transport of methane from the wetland porewater, rather than from *in situ* production in the aquifer. Vertically downward head gradients were observed at various locations in the wetland and at various times of the year (see above section on Characterization of the Hydrogeology). Methane also could have been transported laterally in the aquifer from the upland area, where peat layers were detected in the aquifer (TetraTech, 1999). Although sulfate was present in the aquifer, sulfide was not detected in any samples, providing additional evidence of generally aerobic conditions in the aquifer.

For samples collected from piezometers screened in the wetland sediments (including shallow streambed piezometers), high concentrations of cisDCE relative to TCE concentrations occurred in about half of the piezometers (Figure 2.18a). This indicates that reductive dechlorination is a significant natural attenuation process at some locations in the wetland sediment. Piezometers screened in the wetland sediments did not produce sufficient water to obtain reliable measurements of dissolved oxygen concentrations. In September 2000, highly reducing conditions were indicated in the wetland porewater collected from piezometers by the high methane concentrations (mean of 834 and maximum of 3440 were relatively high  $\mu\text{g/L}$ ) and high sulfide concentrations (mean of 0.28 and maximum of 1.15  $\text{mg/L}$ ) (Table 2.4). A comparison of the piezometer sampling results from September 2000 and March 2001 indicate a seasonal change in the ground-water chemistry that likely was associated with the increased recharge before and during the March 2001 sampling event (Table 2.4). Mean methane concentrations in the wetland piezometer samples decreased by about 60 percent in March 2001 compared to September 2000; mean sulfide concentrations decreased by about 30 percent; and mean sulfate concentrations increased about 30 percent (Table 2.4). These changes in the water chemistry indicate an influx of oxygenated recharge water to the wetland porewater. A corresponding influx of oxygenated water to the aquifer also is indicated by the increase in dissolved oxygen and sulfate concentrations and decrease in ferrous iron and methane concentrations in March 2001 compared to September 2001 (Table 2.4).

### **2.3.2.3 Peeper Sampling in September 2000 and March 2001**

In addition to the piezometers, peepers were placed at sites CM-3, CM-9, CM-13, and ST-4 (in the streambed near CM-13) to obtain detailed vertical profiles of VOCs and redox constituents in the wetland porewater. In September 2000, the peeper samples at each site generally showed the highest TCE concentrations at the deeper sampling points, which are in or near the top of the sand aquifer. TCE concentrations decreased along the upward flowpaths that existed in the wetland sediment in September 2000, and cisDCE concentrations showed a corresponding increase (Figure 2.19). In contrast to the piezometer samples, relatively high cisDCE:TCE ratios were observed in many peeper samples, indicating that anaerobic biodegradation of TCE was occurring in the wetland sediments (Figure 2.18b). The peeper data showed strongly reducing conditions in the wetland porewater in September 2000. Occurrence of cisDCE in the peepers generally coincided with methanogenic zones or mixed methanogenic/iron-reducing zones in the wetland sediment (Figure 2.19). Although these strongly reducing conditions were present in the wetland sediments, TCE dechlorination appeared to be incomplete, stopping at cisDCE. Of all water samples collected in September 2000, the highest methane concentrations were detected in samples collected from peepers placed at sites CM3 and CM9 (PCM3 and PCM9 in Appendix C; Figure 2.19).

The high methane concentrations in the peepers at CM9 and CM3 also coincide with relatively high concentration of toluene, a contaminant that was not detected in other peepers or piezometers. Toluene concentrations at these sites were as high or higher than the TCE concentrations, and benzene also was detected (Figure 2.19). The presence and degradation of these contaminants may have resulted in the relatively high methane concentrations at sites CM9 and CM3, subsequently enhancing biodegradation of the TCE. Toluene, benzene, and other gasoline compounds can serve as carbon substrates for many microorganisms, and they degrade most easily under aerobic conditions. Degradation of BTEX compounds consumes oxygen and other terminal electron acceptors, frequently driving ground water to strongly reducing methanogenic conditions. The source and original extent of toluene and benzene contamination is difficult to determine. Toluene and benzene originally may have been widespread in the aquifer but degraded under the aerobic conditions generally present in the aquifer.

Concentrations of cisDCE and TCE decreased to near or below detection levels before land surface was reached in all peepers in September 2000, except the streambed peeper PST4 (Figure 2.19). The peeper in the streambed (PST4) showed an increase in TCE concentrations at a depth of 12 cm below land surface, followed by another increase in cisDCE concentrations near the streambed surface. Although TCE concentrations were below detection in the streambed peeper PST4 near land surface, cisDCE concentration was about 1.2 :mol/L, or 120 ppb (Figure 2.19). In contrast, surface-water samples at the site where the peeper was placed in the streambed (S13) had concentrations of 0.14 :mol/L (19 :g/L) of TCE and less than 0.01 :mol/L (less than 1 :g/L) of cisDCE. Similarly, relatively high TCE concentrations and undetectable cisDCE concentrations were found in nearby surface-water samples S9, S14, and S15 (Figure 2.17; Appendix C). The contrasting peeper and surface-water concentrations may indicate that TCE is transported to the surface water along preferential flowpaths with high velocity, where less degradation can occur before the surface-water is reached. Similar preferential transport of parent VOCs to surface water has been reported for a PCE plume discharging through river sediments (Conant, 2000). It is unlikely that the higher TCE concentrations compared to cisDCE concentrations in the surface water resulted from preferential volatilization of the cisDCE. Measured Henry's Law constants for cisDCE (299.8 to 453.3 Pa m<sup>3</sup>/mol at 20 °C) are lower than those for TCE (682.8 to 1048 Pa m<sup>3</sup>/mol at 20 °C) (Mackay et al., 1993), indicating that cisDCE has a lower tendency to volatilize.

The wetland porewater chemistry changed greatly in March 2001 compared to September 2000 (Figure 2.19 and 2.20). Total concentrations of TCE and cisDCE decreased substantially in the wetland porewater at most sites in March 2001 compared to September 2000, while the ratio of cisDCE to TCE decreased. For example, cisDCE was the major VOC detected in the peeper at site ST4 in September 2000, with maximum concentrations of about 1.4 :mol/L (Figure 2.19). In contrast, TCE was the major contaminant detected in the peeper at ST4 in March 2001, with maximum concentrations of about 0.14 :mol/L (Figure 2.20). These changes in TCE and cisDCE concentrations in the wetland porewater indicate that contaminant concentrations were diluted and that less anaerobic biodegradation was occurring. An increase in the redox state of the wetland porewater is indicated by the relatively high ferrous iron concentrations and low methane concentrations in most peepers in March 2001 (Figure 2.20). Except for the peeper at site CM3, iron-reducing conditions were predominant in the wetland porewater in March 2001, whereas methanogenic or mixed iron-reducing/methanogenic conditions were observed in September 2000. As noted from the piezometer data, these changes in the water chemistry in the peepers indicate an influx of oxygenated water recharging the wetland in March 2001 compared

to September 2000. Ground-water-flow directions measured in the piezometers (Figure 2.11) indicated that the wetland porewater received oxygenated water directly from precipitation at sites near the wetland/upland boundary (sites CM9 and CM3 in Figure 2.19), and from increased flux of water from the aquifer at sites close to the stream (sites CM13 and ST4 in Figure 2.20).

Although more extensive seasonal sampling and storm event sampling would be needed for a full evaluation, the peeper data presented here indicate that anaerobic degradation of TCE in the wetland sediments at this site decreases during periods of high recharge, causing an increased discharge of TCE to the stream. In peepers at ST4, TCE was below detection levels in September 2000 near the interface of the streambed sediments and surface water (Figure 2.19d), whereas TCE concentrations were 0.14 :mol/L (18.4 :g/L) at this interface in March 2001 (Figure 2.20d). Surface-water concentrations also indicate a higher flux of TCE to the stream in March 2001. At all sites except S-9, surface-water concentrations of TCE remained about the same in March 2001 compared to September 2000, despite the increased volume of water in the stream (Figure 2.17). The water depth in the creek at site ST4 was about 1.2 m in March 2001 compared to about 0.30 m in September 2000. At surface-water site S9, TCE concentrations approximately doubled in March 2001 compared to September 2000 (Figure 2.17).

### **2.3.3 Microcosm Evidence of Biodegradation**

Microcosms constructed with wetland sediment collected near site CM13 showed that anaerobic biodegradation of TCE is slow compared to the wetland sediments at the APG study area (Figure 2.21). In TCE-amended microcosms constructed with wetland sediment from Colliers Mills, no evidence of TCE biodegradation was observed over the 35-day incubation period. The decrease in TCE concentrations in live and sterile microcosms with the Colliers Mills sediment were about the same, and production of cDCE and VC was not observed (Figure 2.21a). The laboratory microcosms constructed with wetland sediment from APG showed rapid anaerobic degradation of TCE and production of cisDCE and VC (Figure 2.21a), as observed in earlier microcosm experiments (Lorah et al, 2001). The loss of TCE in the sterile and live microcosms is most likely due to sorption to the organic-rich sediments. Although all microcosms were amended with the same concentration of TCE at day 0, the Colliers Mills microcosms had less than half the TCE concentration at day 3 than that in the APG microcosms. Sorption, therefore, appears to be higher in the Colliers Mills wetland sediment than the APG wetland sediment. Insignificant loss of TCE was observed in water controls during the microcosm experiment, showing that volatilization and sorption to the bottle or Teflon-coated rubber stoppers was minimal (data not shown).

The wetland sediments for these microcosms were collected in September 2000, when porewater samples at site CM13 showed evidence of anaerobic degradation of TCE to cisDCE and of methane production. The Colliers Mills microcosms, therefore, may have degraded the TCE after a longer period of incubation. Production of ferrous iron in the microcosms indicated anaerobic conditions (Figure 2.21b), but methane production did not occur over the 35-day incubation in the Colliers Mills microcosms. Methane concentrations in the APG microcosms amended with TCE increased from about 100 to 900 :mol/L over the incubation period, whereas methane concentrations in the Colliers Mills microcosms remained below detection (data on file, U.S. Geological Survey, Baltimore, Maryland). Based on the field data alone, the possibility of

VC and 12DCE degradation under iron-reducing conditions without accumulation in the porewater could not be excluded (Bradley and Chapelle, 1996). However, the negligible TCE degradation observed in the Colliers Mills microcosms (Figure 2.21), makes this possibility seem unlikely.

#### **2.3.4 Evidence of Sorption**

Sorption and evapotranspiration are two physical attenuation processes that could affect movement of the chlorinated solvents through the wetland sediments and decrease concentrations in the porewater. To evaluate sorption of the wetland sediments, sediment samples were collected at depth intervals of 3 cm or less at sites SS2 and SS3, which were located near piezometer sites CM3 and CM9, respectively, and analyzed for VOCs after methanol extraction (Table 2.5). Large organic material in the sediment made it difficult to obtain sediment cores in the wetland sediment. At site SS2, wetland sediment samples were obtained only between depths of 39.6 and 56.4 cm; the remaining sediment samples at this site consist of sand (Appendix C).



Table 2.5. Volatile organic compounds measured by methanol extraction of sediment core samples collected from SS2 and SS3 on March 12 and 13, 2001, respectively (see Figure 2.2)

[D, duplicate sample; cm bls, centimeters below land surface; µg/L, micrograms per liter; <, less than]

Sedi- ment type	Depth (cm bls)	Trichlo ro- ethene (µg/L)	<i>cis</i> - 1,2- Dich loro- ethene (µg/L)	1,1- Dichloro- ethene (µg/L)	Toluene (µg/L)	<i>p</i> - Isopropyl- toluene (µg/L)	<i>n</i> - Butyl- benzene (µg/L)	Napthalene (µg/L)
<b>Sediment Core SS2</b>								
peat	39.6-42.7	<25.0	<25.0	<25.0	<25.0	128	<25.0	40.3
peat	42.7-45.7	<25.0	<25.0	<25.0	<25.0	84.5	<25.0	<25.0
peat	48.8-50.3	1010	<25.0	<25.0	<25.0	72.3	<25.0	<25.0
peat	50.3-51.8	1130	<25.0	<25.0	<25.0	46.7	<25.0	<25.0
peat	51.8-53.3	2680	<25.0	<25.0	182	182	<25.0	<25.0
peat	D 51.8-53.3	3040	<25.0	<25.0	210	195	<25.0	<25.0
peat	53.3-56.4	34.5	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	61.0-61.9	45.2	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	67.1-68.6	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	D 67.1-68.6	27.5	<25.0	<25.0	<25.0	<25.0	<25.0	66.1
sand	73.2-74.7	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	D 73.2-74.7	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	79.2-80.8	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	D 79.2-80.8	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	85.3-86.9	<25.0	<25.0	<25.0	<25.0	39.6	54.6	<25.0
sand	D 85.3-86.9	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	91.4-93.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	D 91.4-93.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	97.5-99.1	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
sand	D 97.5-99.1	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
<b>Sediment Core SS3</b>								
peat	76.2-77.7	68.7	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	79.2-80.8	72.2	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	80.8-82.3	79.4	37.8	27.4	<25.0	162	<25.0	<25.0
peat	83.8-85.3	45.6	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	D 83.8-85.3	43.6	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	88.4-89.9	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	D 88.4-89.9	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	94.5-96.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	D 94.5-96.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	100.6-102.1	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	D100.6- 102.1	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	106.7-108.2	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	D106.7- 108.2	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	112.8-114.3	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
peat	D112.8- 114.3	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0

TCE, toluene, and *p*-isopropyl-toluene were the most frequently detected contaminants in the soil samples and occurred in the highest concentrations (Table 2.5). TCE concentrations were greatest at site SS2 between 48.8 and 53.3 cm below land surface in the peat, ranging between about 1,000 and 3,000 :g/L in the methanol extractions (Table 2.5). These TCE concentrations are about 20 to 60 times greater than sorbed concentrations (as determined by methanol extractions) in the sand aquifer underlying the peat at site SS2. TCE concentrations were 27.5 and 45.2 :g/L in two sand samples (Table 2.5). Comparison of the methanol-extracted concentrations to concentrations measured in aqueous samples indicates a high sorption capacity of the wetland sediments, although sorption coefficients cannot be calculated from samples that were not collected at the same time or the exact same location. At nearby site CM3, a piezometer screened at a depth of 21 cm in the wetland sediment had 5.4 :g/L TCE and 16.8 :g/L toluene in March 2001, within 2 weeks of collecting sediment samples.

At site SS3, all the sediment samples collected were in the peat layer, but samples were obtained only between depths of 76 and 114 cm below land surface. TCE concentrations at SS3 ranged between 43.6 and 79.4 :g/L at depths of 76 to 85 cm, and *p*-isopropyl-toluene concentration was 162 :g/L at depths of 80.8 to 82.3cm. In CM9-3T, which is the closest piezometer screen to these soil cores, aqueous TCE concentration was 60.7 :g/L in March 2001, implying a much lower ratio of sorbed to aqueous TCE concentrations than observed at site SS2. The relatively narrow depth interval at which TCE was detected by methanol extraction of the sediment at SS2 and SS3 indicates a large spatial heterogeneity in sorption in the wetland sediments.

Batch sorption tests to determine distribution coefficients ( $K_d$ 's) were not conducted with sediment from the Colliers Mills WMA, but the microcosm tests can be used to obtain an estimate of the  $K_d$  for TCE. Microcosms were amended with 1,200  $\mu\text{g/L}$  of TCE (9.12  $\mu\text{mol/L}$ ) at day 1, and this initial concentration was confirmed by analyses of water controls that did not contain sediment. However, at day 1 in the live microcosms with wetland sediment from site CM13, the TCE concentration was only 308  $\mu\text{g/L}$  (2.34  $\mu\text{mol/L}$ ), although degradation products were not observed throughout the incubation (Figure 2.2.1). By day 6, the TCE concentration reached 66  $\mu\text{g/L}$  (0.50  $\mu\text{mol/L}$ ) and remained approximately the same for the remaining 29 days of incubation, indicating that sorption equilibrium had been reached (Figure 2.21). If 66  $\mu\text{g/L}$  of TCE was in solution at equilibrium, then 1134  $\mu\text{g/L}$  was sorbed to the wetland sediment. The ratio of the sorbed and aqueous TCE concentrations gives a  $K_d$  of 17 for the Colliers Mills WMA wetland sediment. In contrast, the  $K_d$  for TCE in wetland sediment from the APG wetland site is about 2.0, using the aqueous and estimated sorbed concentration in the microcosms at day 3 [after day 3, degradation products are observed and sorption can not be discerned] (Figure 2.21). This  $K_d$  for TCE is in the range of those calculated previously for 1,1,2,2-tetrachloroethane, *cis*-12DCE, and *trans*-12DCE in 24-hr batch sorption tests with the APG wetland sediment (Lorah et al., 1997). Thus, the Colliers Mills WMA wetland sediment has a substantially higher sorption capacity than the APG wetland sediment.

The estimated  $K_d$  for TCE can be used to calculate the coefficient of retardation,  $R$ , which is defined as the ratio of the average linear ground-water velocity to the average velocity of the contaminant.  $R$  can be calculated from

$$R = 1 + (P_b K_d)/n$$

where

$P_b$  is the bulk mass density [ $P_b = P_s (1-n)$  where  $P_s$  is the particle mass density];  
 $K_d$  is the distribution coefficient; and  
 $n$  is porosity.

If a particle mass density of  $2.65 \text{ g/cm}^3$  and porosity of 0.4 is assumed for the wetland sediment,  $P_b$  is  $1.59 \text{ g/cm}^3$  and  $R$  is about 68.  $R$  of 68 indicates that rate of movement of TCE through the wetland sediment is 68 times slower than the advective ground-water flow because of sorption. Using the average linear velocity of about 0.12 m/yr that was estimated for advective ground-water flow in the Colliers Mills WMA wetland sediments (see Section 2.3.1.4), the velocity for TCE transport in the wetland sediment would be about 0.0018 m/yr. However, flow velocity (and thus contaminant transport) could be an order of magnitude higher throughout much of the wetland sediment because of the presence of tree roots and lenses of coarse and gravel (see Section 2.3.1.4).

### 2.3.5 Evidence of Phytoremediation

Water-level and tree core data indicate that phytoremediation by tree uptake of VOCs could be a major natural attenuation process in this forested wetland. Water-level data show the amount of uptake of ground water by vegetation in the wetland, and tree core analyses show that TCE is transported through the trees with this water uptake. Continuous water-level measurements in piezometers show evidence of diurnal effects from evapotranspiration throughout the warmer months of the year (Figure 2.12). Water levels declined during the day as a result of phreatophytic consumption and then recover during the night when the plant stomata are closed (Freeze and Cherry, 1979). Figures 2.22 and 2.23 show hydrographs for 72-hour periods that clearly show this diurnal cycle. At sites CM9 and CM13, daily fluctuations began in late April and continued through mid-October when the effects were visibly beginning to abate. Prior to late April and before plants are actively growing, diurnal changes were minimal (Figures 2.22 and 2.23). The maximum amplitude of the diurnal cycles occurred in late July and early August (Figures 2.22 and 2.23). At both sites, the lowest water levels within a 24-hr period occurred in the late afternoon, roughly from 1500 hrs to 1900 hrs, although these times varied according to antecedent moisture conditions. The highest water levels within a 24-hr period occurred in the early morning hours, roughly between 0500 hrs and 0900 hrs. These troughs and peaks correspond, with a slight lag time, to times of maximum and minimum vegetative uptake, respectively.

The CM9 wells showed a greater diurnal change (higher amplitude) than the CM13 wells. The difference may be attributed to the different types of vegetative species at the two sites. The CM9 wells are located in a mixed stand of young cedars and deciduous trees (primarily oak, maple, and beech) where some sunlight is able to filter through to the land surface during maximum leaf coverage. The CM13 wells are located in a dense stand of mature cedars where most of the sunlight is prevented from reaching the land surface during all seasons of the year. Huber (1953) found that the relative rates of transpiration were between 1.5 and 5 times greater in oak and beech leaves than in various pine species. The relatively smoother and less accentuated water-level peaks and troughs at the CM13 site compared to those at the CM9 site also may be attributed in part to species differences. Generally, pines transpire for longer time periods than deciduous trees, and although pines may transpire less on a "leaf-by-leaf" basis per tree, as a dense stand they may have a larger impact on the ground water by intercepting more precipitation before it reaches the ground (J.M. Vose, U.S. Department of Agriculture Forest

Service, Otto, North Carolina, oral communication, 2001). Besides species differentiation however, many environmental factors can influence the rate and cyclic patterns of water uptake. Some of these factors include light, temperature, stocking (canopy, or leaf coverage), CO<sub>2</sub> concentration of the air, water supply, air humidity, soil composition, microbial populations in the rhizosphere, pollutants, insects, diseases, and various interactions among these components (J.M. Vose, U.S. Department of Agriculture Forest Service, Otto, North Carolina, personnel communication, 2001; Kozlowski and Pallardy, 1997).

As indicated by the amplitudes, diurnal response was the greatest in piezometers screened in the aquifer at 3- to 3.6-m depths below land surface. The 0.6- to 0.9-m deep piezometers screened in the wetland sediment also showed diurnal change, but to a slightly lesser degree. It is likely that the depth of most of the tree roots extend no greater than a few meters below land surface, with most of the roots at or just below the aquifer-wetland sediment interface. Because the wetland sediments have a lower hydraulic conductivity than the aquifer sediments, the diurnal effect may not be fully transmitted to the shallower piezometers. In addition, the diurnal effect does not extend to depths of 6 m in the aquifer, as indicated by the steady water levels in the deepest piezometer at CM13 (Figure 2.23). It also is possible that there is little hydrologic connection between the 3.6-and 6.4-m depths at site CM13. A thin silt/clay layer is present between the two depths at this site (Appendix C) and could explain the lack of response in the deeper piezometer. Continuous water-level measurements were not made in any other deep wells.

Tree core analyses showed the presence of TCE in cedar trees in the wetland, providing evidence that transport of water through the trees also transports VOCs (Figure 2.24). Concentrations in the tree cores correlate well to concentrations in the ground water in nearby piezometers (Figure 2.24). Where contamination was not detected in the ground water, such as at CM14, TCE was not detected in the tree core. Diurnal fluctuations in water levels indicated that tree uptake of VOCs could occur during late April to mid-October. TCE was the only VOC detected in the tree cores, although cisDCE was detected in the shallow ground water at several of these sites. Diurnal fluctuations in water levels indicated that the tree roots are drawing water primarily from the aquifer or near the wetland sediment/aquifer interface, where concentrations of the anaerobic daughter product cisDCE was low or undetectable. Because cisDCE has a lower tendency to volatilize than TCE (see Section 2.3.2.2), it is unlikely that cisDCE is not detected in the trees because of preferential transport to the air. It is unknown whether any degradation of the TCE occurs during uptake and transport through the tree.

## 2.4 Comparison to the Tidal Freshwater Wetland Site (Aberdeen Proving Ground, Maryland) and Implications for Natural Attenuation as a Remedy

The field and laboratory evidence show that anaerobic biodegradation is less efficient in the Colliers Mills wetland sediment than in the APG wetland sediment. The absence of VC production indicates that biodegradation is incomplete in the Colliers Mills wetland sediments, even when methanogenic conditions occurred. High DOC concentrations in the organic-rich wetland and creek-bed sediments indicate that organic substrate concentration is not a limiting factor in TCE degradation. DOC concentrations in peeper samples at site ST-4, for example, ranged from 5 to 79 mg/L in September 2000, with a median concentration of 29 mg/L (Appendix C). Wetland porewater samples from piezometers had mean DOC concentrations of 17 to 18 mg/L (Table 2.3). In addition to the high natural organic carbon present in the wetland porewater, toluene and benzene, which also can provide a carbon substrate for reductive dechlorination of chlorinated solvents, were present in the wetland porewater at some sites (Figure 2.20). Although the sites with benzene and toluene also had the highest methane concentrations, degradation of TCE past cisDCE still did not occur.

The less efficient chlorinated solvent degradation in the wetland sediments at the Colliers Mills site most likely can be attributed partly to differences in ground-water residence time in the wetland sediment, and partly to differences in the microbial communities that are active in the wetland. Estimated average linear velocity in the aquifer at the Colliers Mills site is about 2 m/yr along upward flowpaths (see section 2.3.1.4), whereas the upward ground-water flow velocity is between 0.6 to 0.9 m/yr at the APG site (Lorah and Olsen, 1999b). Although calculated linear flow velocities in the wetland sediment at the Colliers Mills site was similar to that at the APG site, the tree roots and large wood debris in the peat at the Colliers Mills site greatly increase the potential for macropore flow. Flow in macropores could bypass anaerobic zones in the wetland sediment where natural attenuation through reductive dechlorination would occur. Macropore transport of contaminants could explain in part the relatively high TCE concentrations (Figure 2.17) observed in Success Branch even during periods when methanogenic conditions and production of cisDCE were observed in the peepers. The thinner wetland sediments at Colliers Mills (0.3 to 1.2 m) compared to the wetland sediments at APG (1.8 to 3.6 m) also would result in a lower residence time for the contaminants in the Colliers Mills wetland sediments, giving less time for degradation to occur.

If the difference in natural attenuation efficiency at the two sites was caused solely by hydrologic factors, however, similar biodegradation rates would be expected in the two sets of laboratory microcosms (Figure 2.21). The insignificant degradation in the Colliers Mills microcosms compared to the APG microcosms indicates that the active wetland microbial communities differ at the two sites, and that microbial species or groups critical for rapid biodegradation are lacking or inactive at the Colliers Mills site. The periodic increase in redox state of the wetland porewater from influx of oxygenated rainwater most likely is a dominant factor on the microbial communities in the Colliers Mills wetland sediments. Such a dramatic change in redox conditions as was observed between the September 2000 and March 2001 sampling periods at Colliers Mills has not been observed in the APG wetland sediment. A recent laboratory study with an anaerobic microbial consortium that reductively dechlorinates TCE to ethene found that the organisms that catalyze the final dechlorination step are extremely sensitive to oxygen (Richardson et al., 2002). This study suggested that transient oxygen exposure could

alter subsurface microbial communities, causing incomplete TCE reductive dechlorination (Richardson et al., 2002). Factors such as the acidic nature of the wetland porewater at Colliers Mills compared to APG sediments and the different type of vegetation and, thus, the type of available organic substrate, also would result in different microbial communities in the wetland sediments at the two sites.

The comparison of the Colliers Mills WMA and the APG wetland sites shows that natural attenuation of chlorinated solvents may not be efficient at all wetland sites, despite organic-rich characteristics of the sediment. Insufficient supply of electron donors often has been cited as the primary reason for incomplete reductive dechlorination of chlorinated solvents (National Research Council, 2000), but the results of this wetland study indicate that microorganisms with the necessary degradative capabilities are the first requirement. A number of recent studies have shown that complete degradation of TCE requires the presence of specific dechlorinating bacteria and that bacterial populations capable of degradation may be present at one site and not at others (Harkness et al., 1999; Ellis et al., 2000; Haack and Bekins, 2000). Dechlorinating bacteria of the *Dehalococcoides* and *Desulfuromonas* groups have been detected in the APG wetland sediments using specific primers (Lorah et al., in press), but similar molecular analyses have not been done with the Colliers Mills WMA wetland sediments. Additional microbiological studies of these wetland sediments could lead to a better understanding of the factors required for growth of dechlorinating bacteria.

Although anaerobic biodegradation in the Colliers Mills WMA wetland sediments is not complete, sorption and plant uptake also attenuate TCE as it moves from the aquifer and through the wetland sediments. The retardation factor for the Colliers Mills wetland sediment was estimated to be nearly 70, compared to about 10 in the less organic-rich APG wetland sediments. Although tree uptake of TCE also occurred, hydrologic data indicate that this attenuation mechanism probably is significant only about 6 months of the year. Because of the seasonal and recharge effects on biodegradation and plant uptake, a more complete seasonal and storm-related study would need to be completed at this wetland site to fully evaluate the feasibility of natural attenuation as a remediation method for the TCE plume. The doubling in TCE concentrations at one surface-water sampling site in March 2001 compared to September 2000 show the effect that high recharge events can have on TCE flux to the stream (Figure 2.17). In contrast, the hydrology and geochemistry in the wetland sediments at APG do not respond to individual recharge events, and strongly reducing conditions are maintained throughout the year. Tidal fluctuations in ground-water-flow directions in the APG wetland sediments act to increase residence times in the wetland porewater, thereby increasing biodegradation, rather than the decrease in biodegradation observed with precipitation events at Colliers Mills. Thus, this demonstration indicates that precipitation-dominated wetlands may provide less suitable conditions for natural attenuation of chlorinated solvents than tidal wetlands.



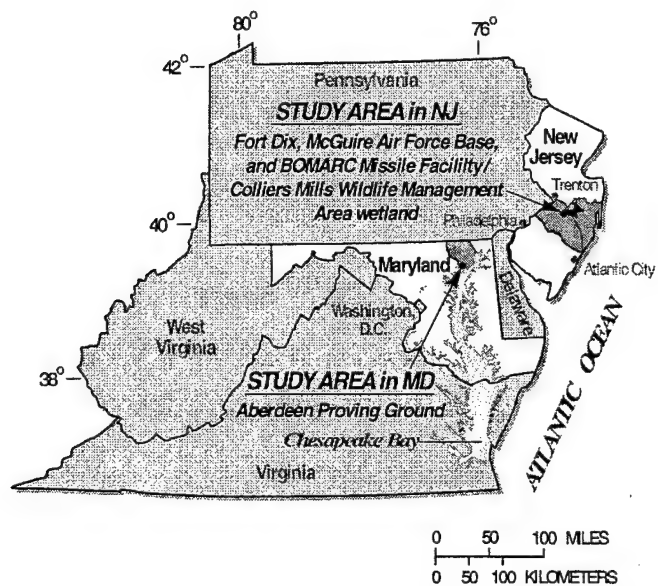
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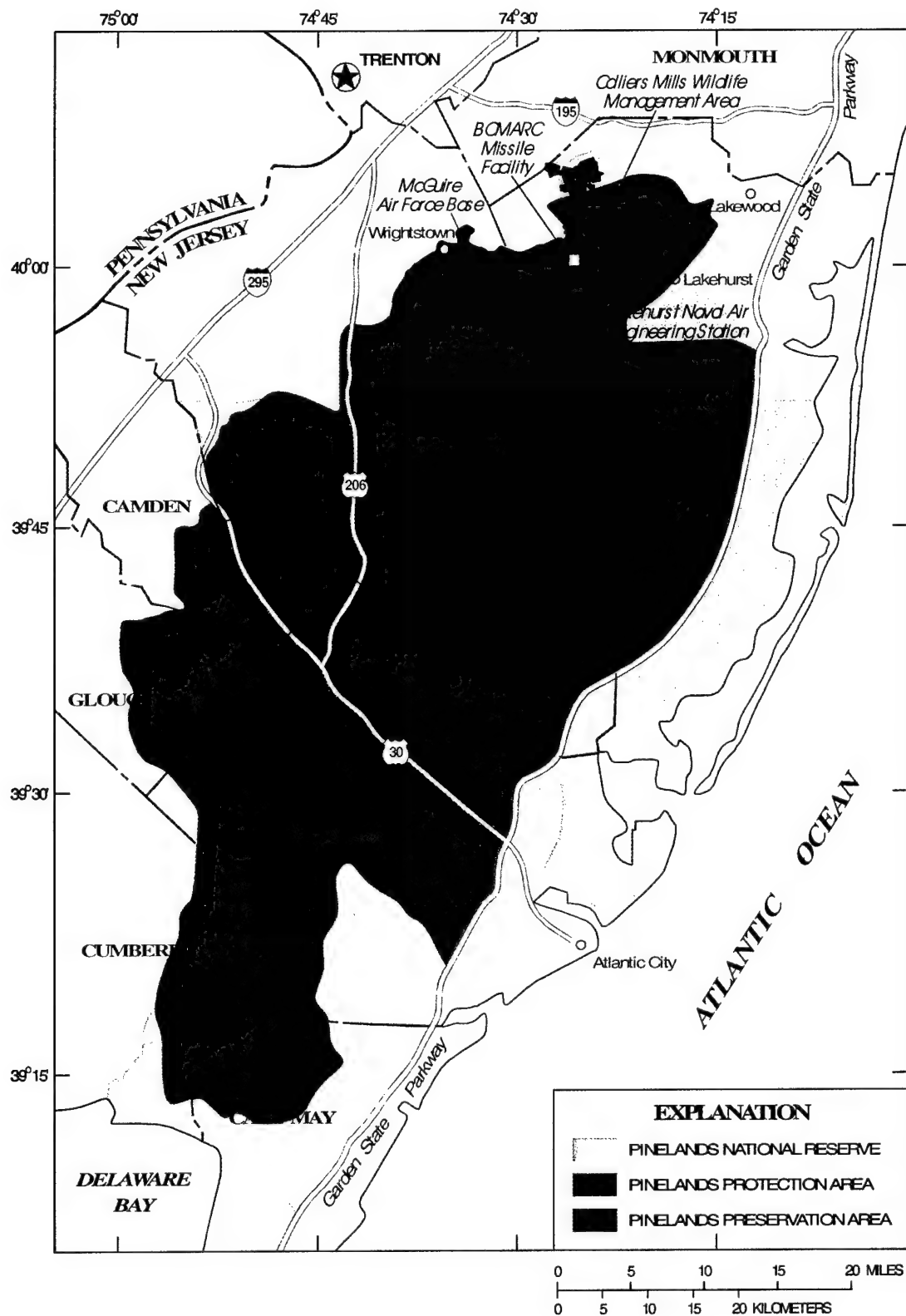


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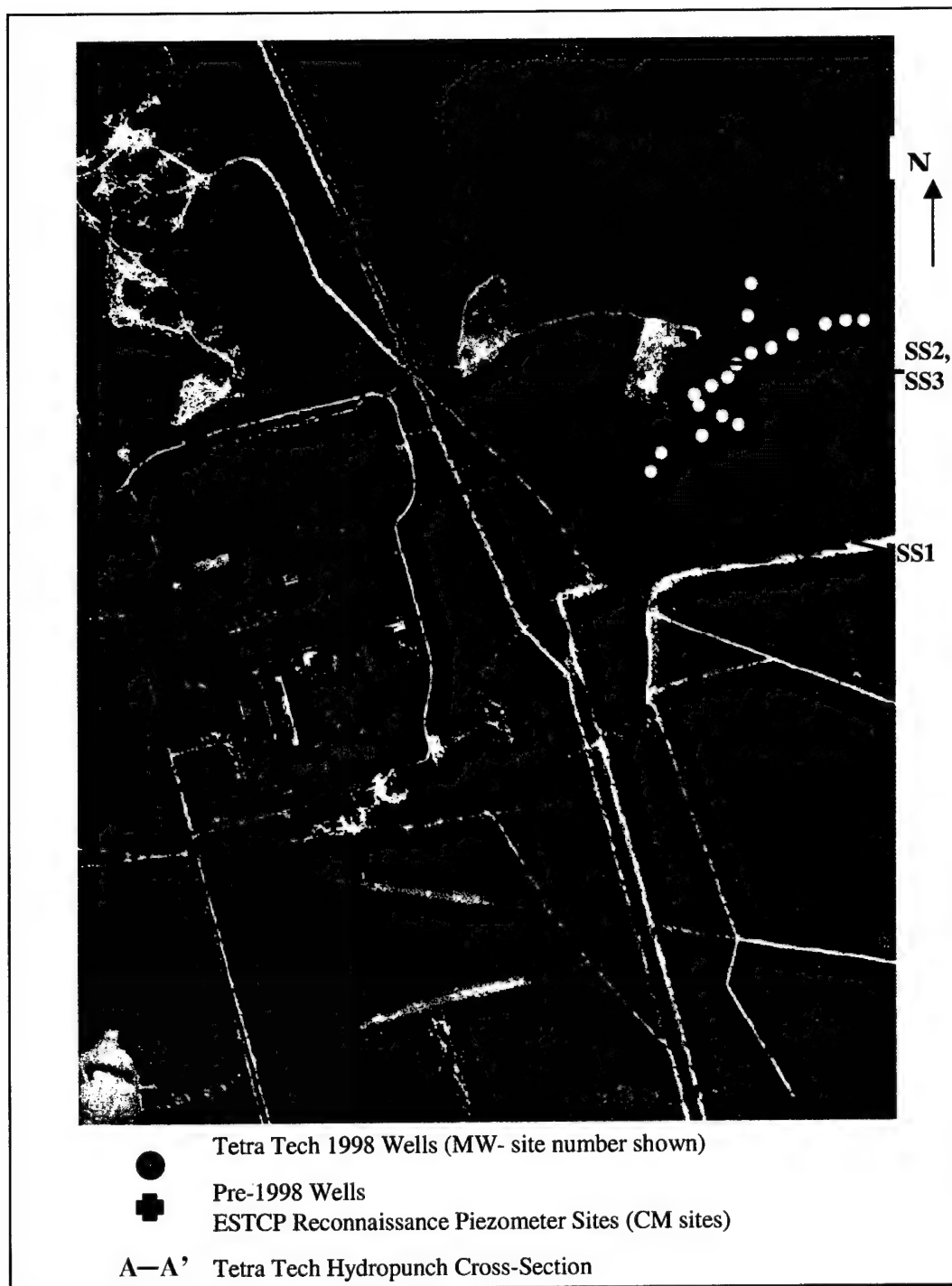
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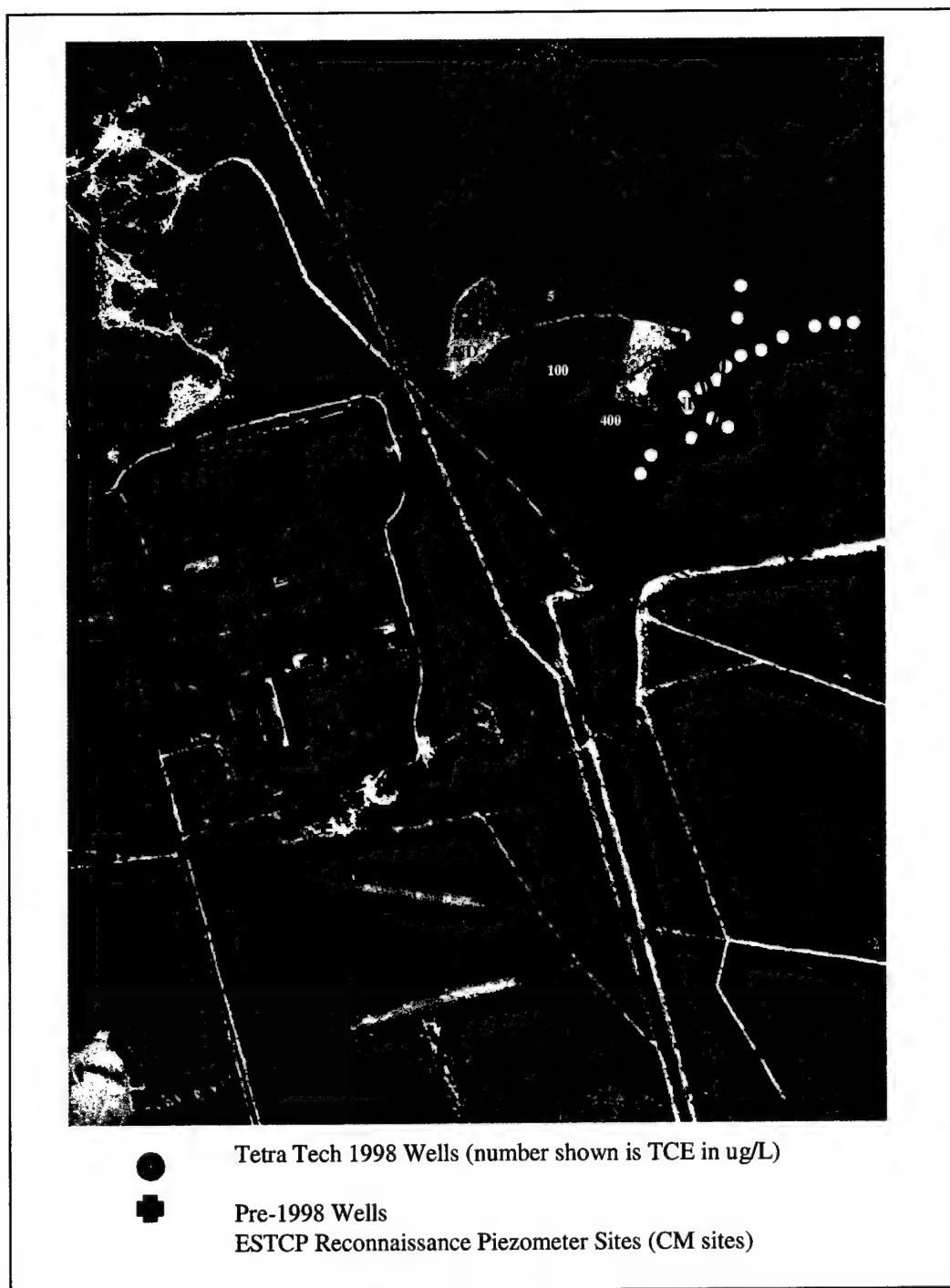
**Figure 2.1a.** Location of Fort Dix Military Reservation, McGuire Air Force Base, and the BOMARC Missile Facility/Colliers Mills Wildlife Management Area wetland study area, Burlington and Ocean Counties, New Jersey, and Aberdeen Proving Ground study area, Harford County, Maryland.



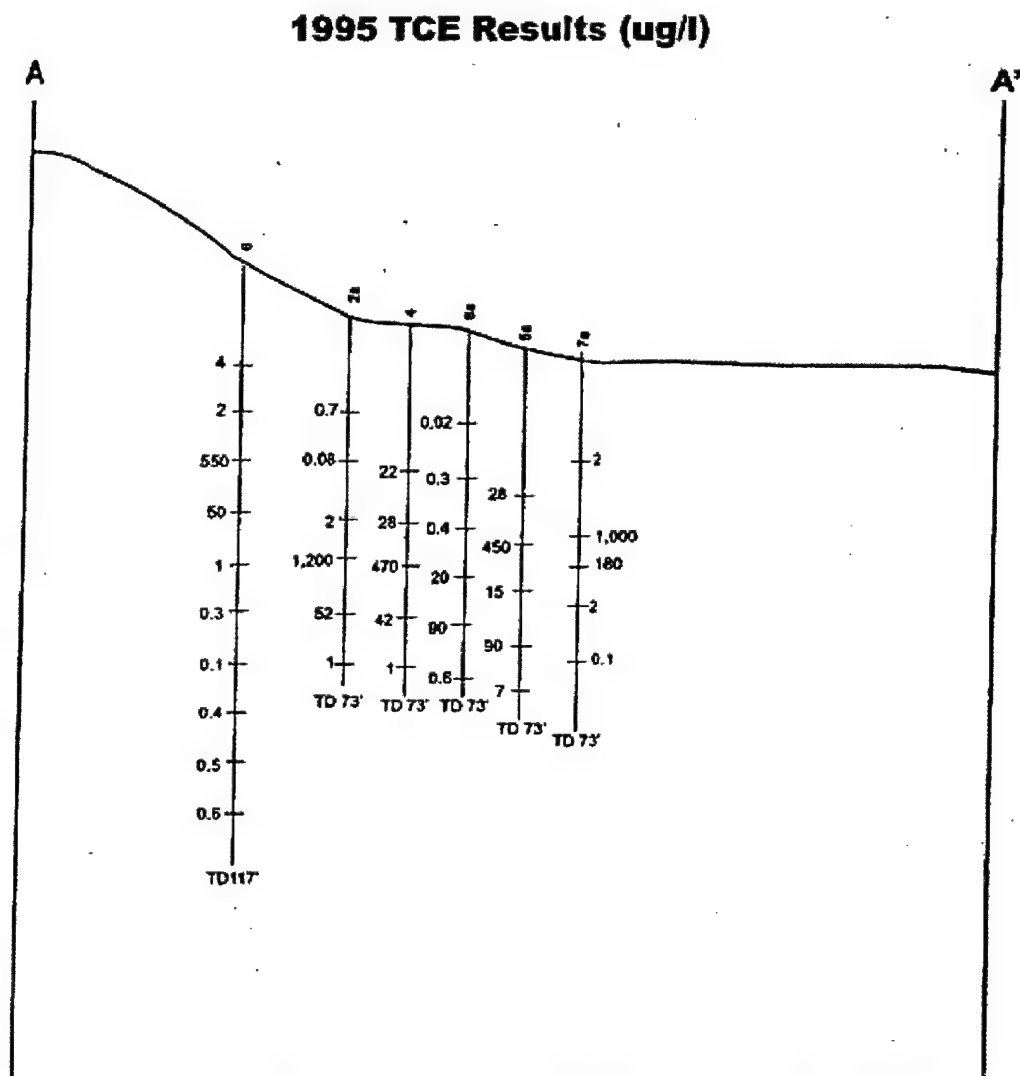
**Figure 2.1b.** Location of Fort Dix Military Reservation, McGuire Air Force Base, and the BOMARC Missile Facility/ Colliers Mills Wildlife Management Area wetland study area, Burlington and Ocean Counties, New Jersey, and the Pinelands National Reserve.



**Figure 2.2.** Locations of the BOMARC Missile Facility/Colliers Mills Wildlife Management Area (WMA) wetland study site, including ESTCP piezometer and sediment core sites, existing Tetra Tech wells, and Tetra Tech Hydropunch A-A' cross-section (Tetra Tech, 1999). SS1, SS2, and SS3 (purple triangles) mark sediment core locations.

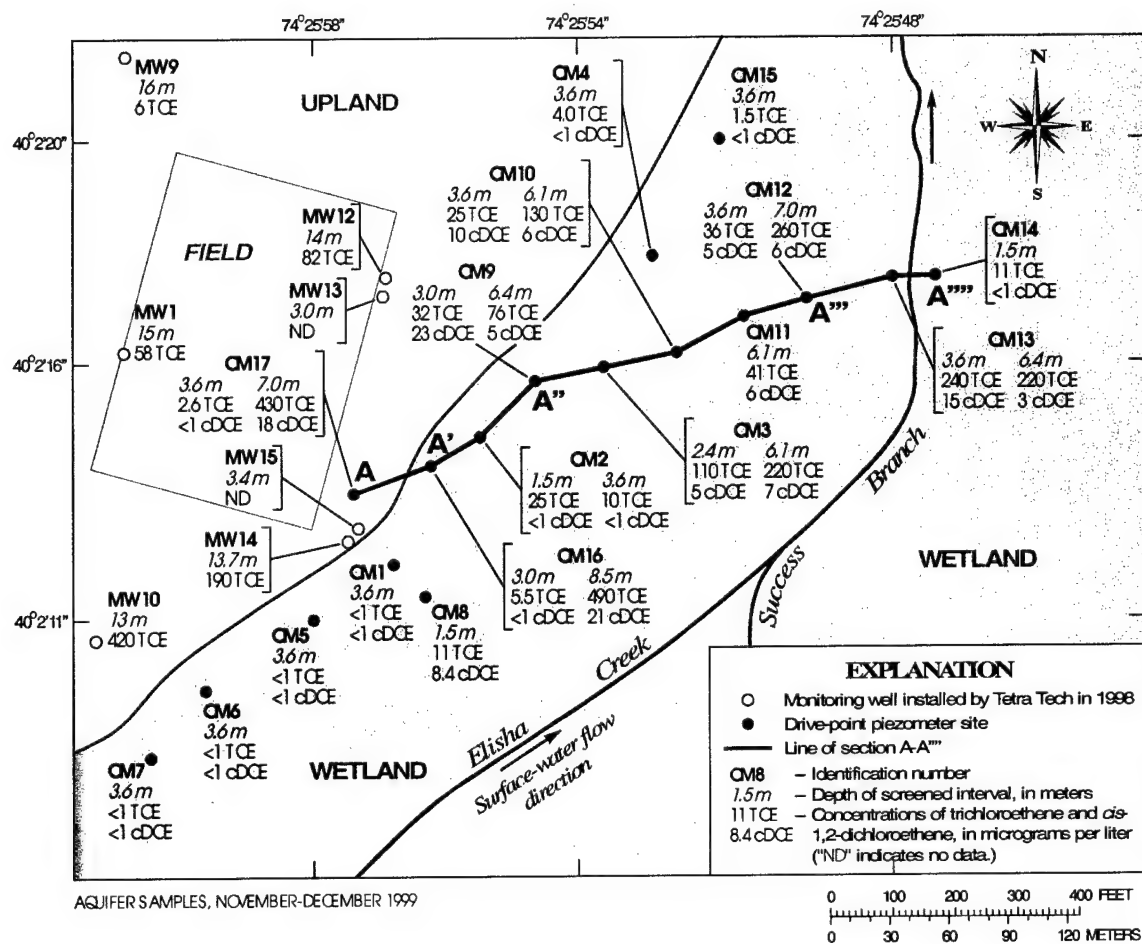


**Figure 2.3.** TCE plume defined by Tetra Tech (1999) at the BOMARC Missile Facility. Note that plume contours were based only on previous sampling by Tetra Tech of existing 1998 wells and do not include sampling done for this ESTCP study.



**Figure 2.4.** TCE concentrations in ground water along section A-A' from Tetra Tech 1995 Hydropunch borings [Tetra Tech (1999)]. Note that A' is immediately west of the wetland study area (see Figure 2.2).





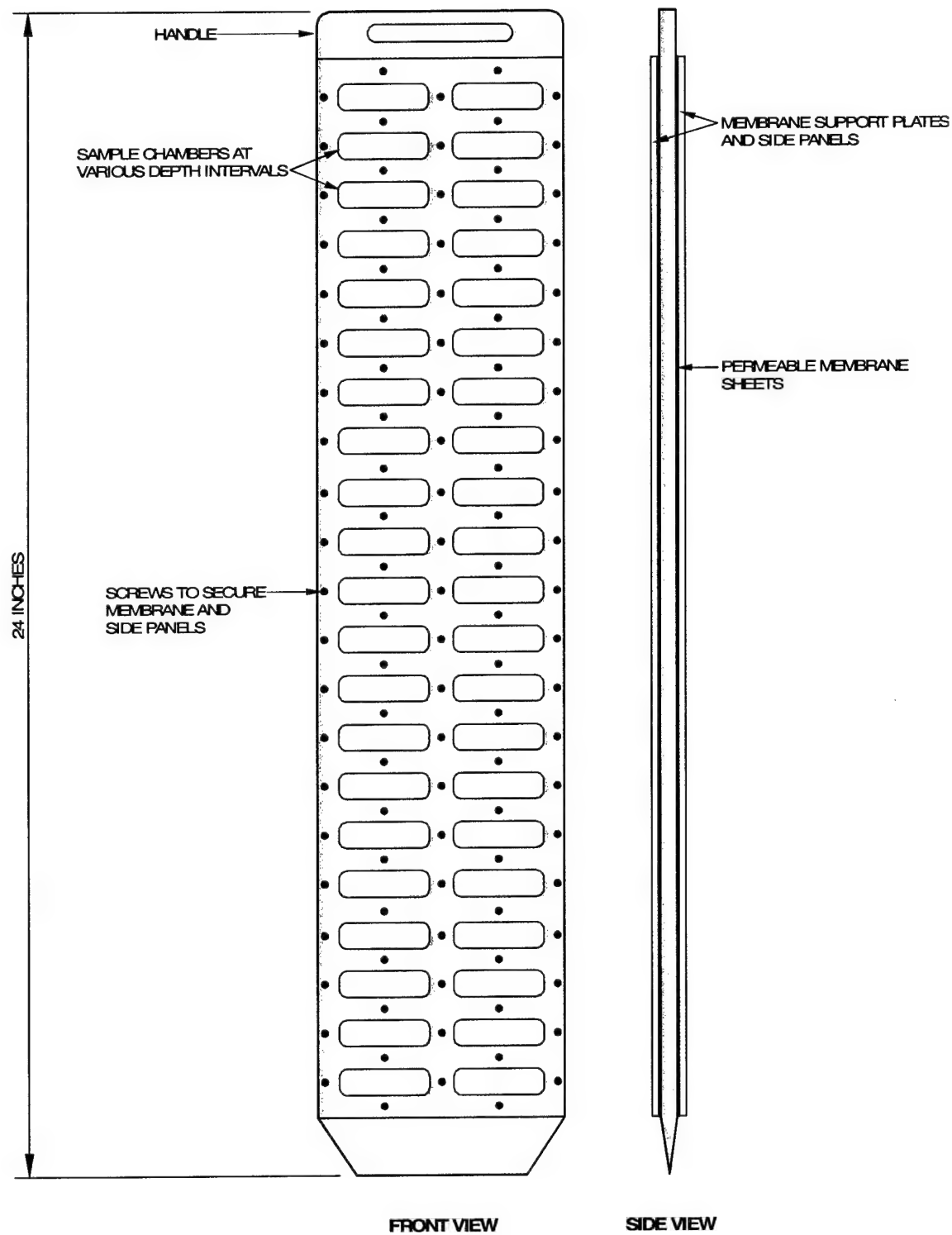
**Figure 2.5.** Locations of piezometers screened in the aquifer at the ESTCP demonstration area at BOMARC Missile Facility / Colliers Mills Wildlife Management Area wetland site, concentrations of trichloroethene (TCE) and *cis*-1,2-dichloroethene (cDCE) determined during reconnaissance-phase sampling, November-December 1999, and line of section A-A'''.

[Screen depth noted is the depth in meters below ground surface of the bottom of the screened interval (0.15 m screened interval in all CM piezometers).]

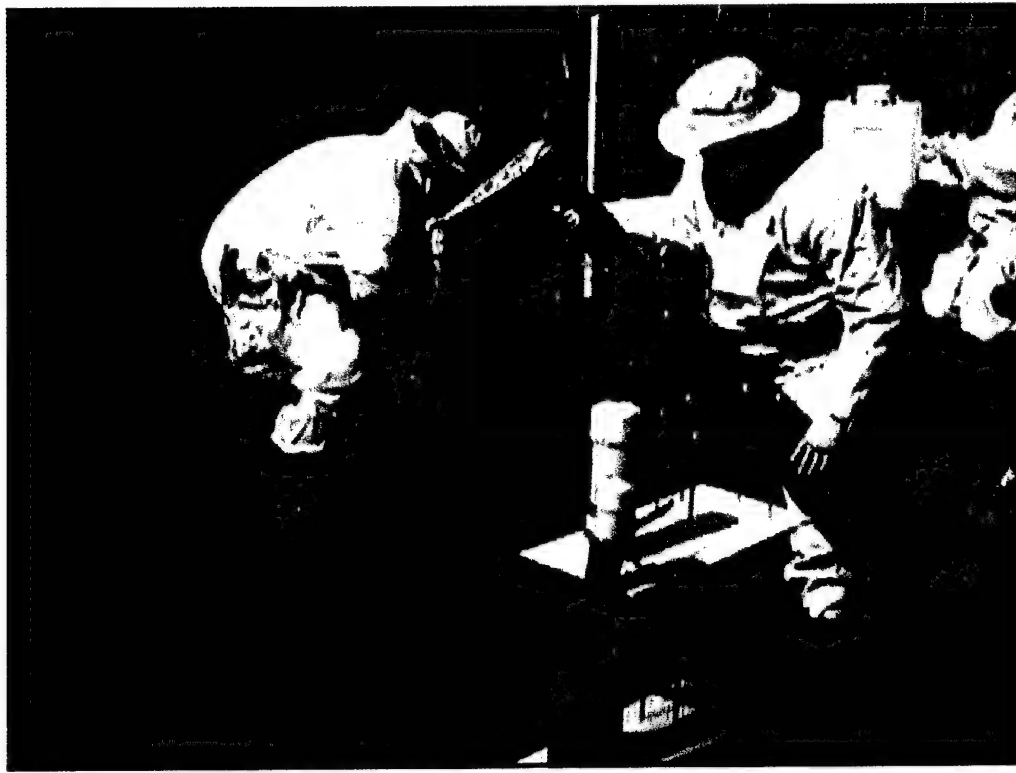




**Figure 2.7.** Direct push GeoProbe rig mounted onto a John Deere Gator. This drill rig was used at the Colliers Mills WMA wetland site at McGuire AFB, NJ to obtain sediment cores and install drive-point piezometers.



**Figure 2.8.** Schematic diagram of a porous-membrane sampling device. (From Spencer et al., 2000)



**Figure 2.9** Photograph of peeper extraction. [at USGS APG wetland site]

## Cross-Section (MW10 to CM18)

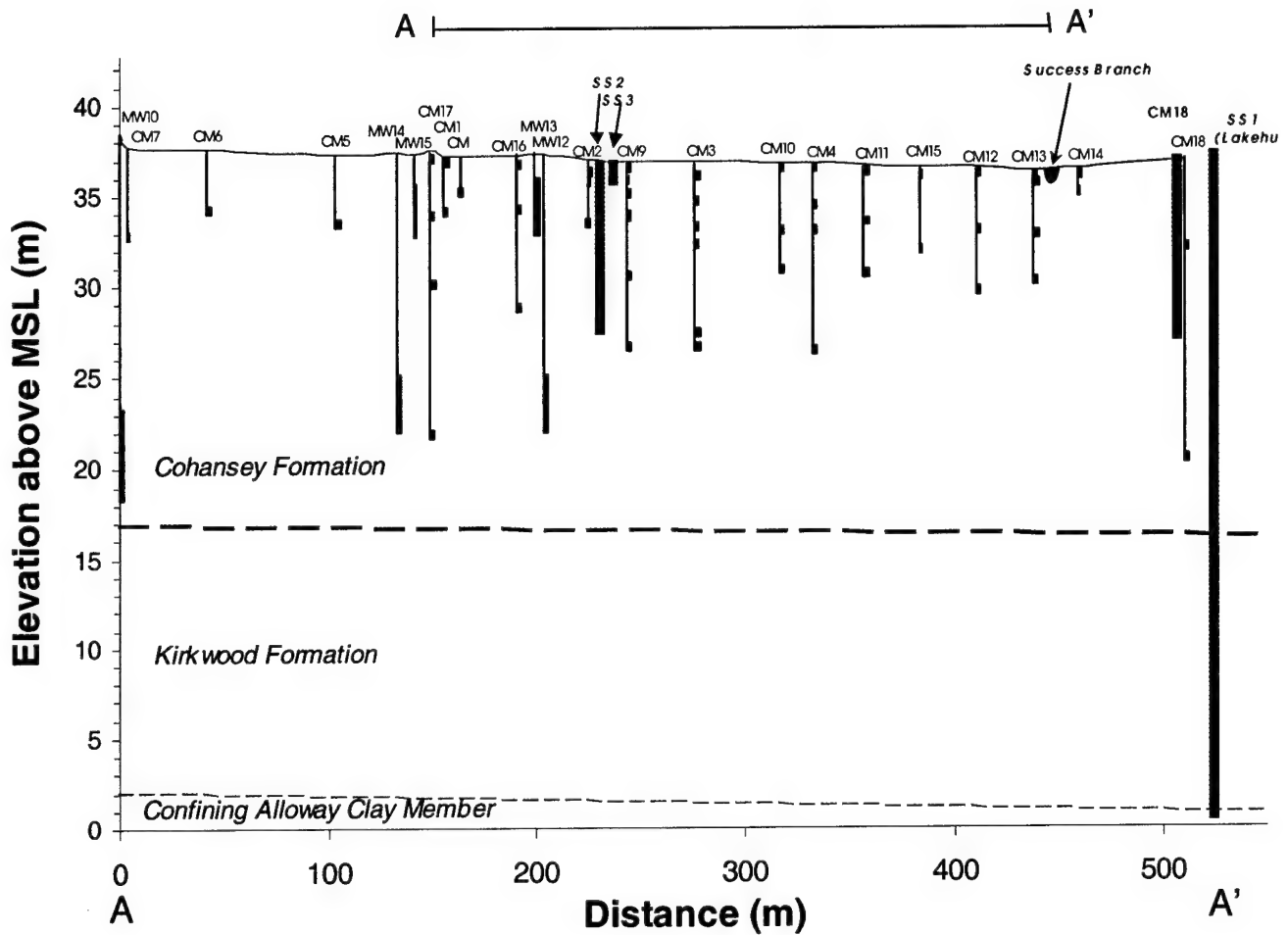
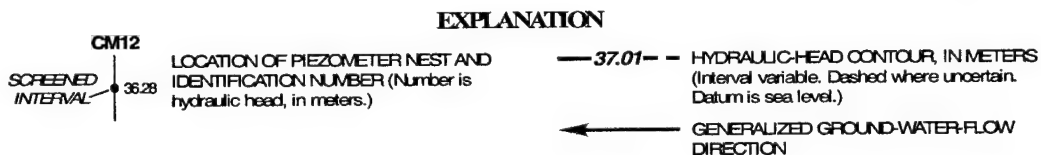
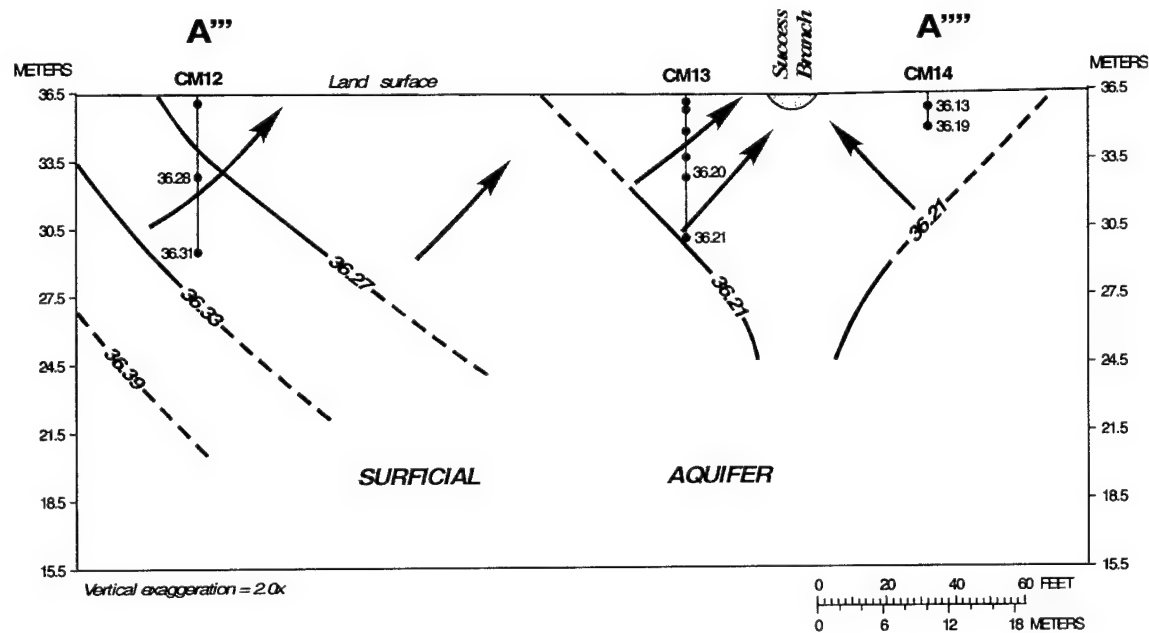
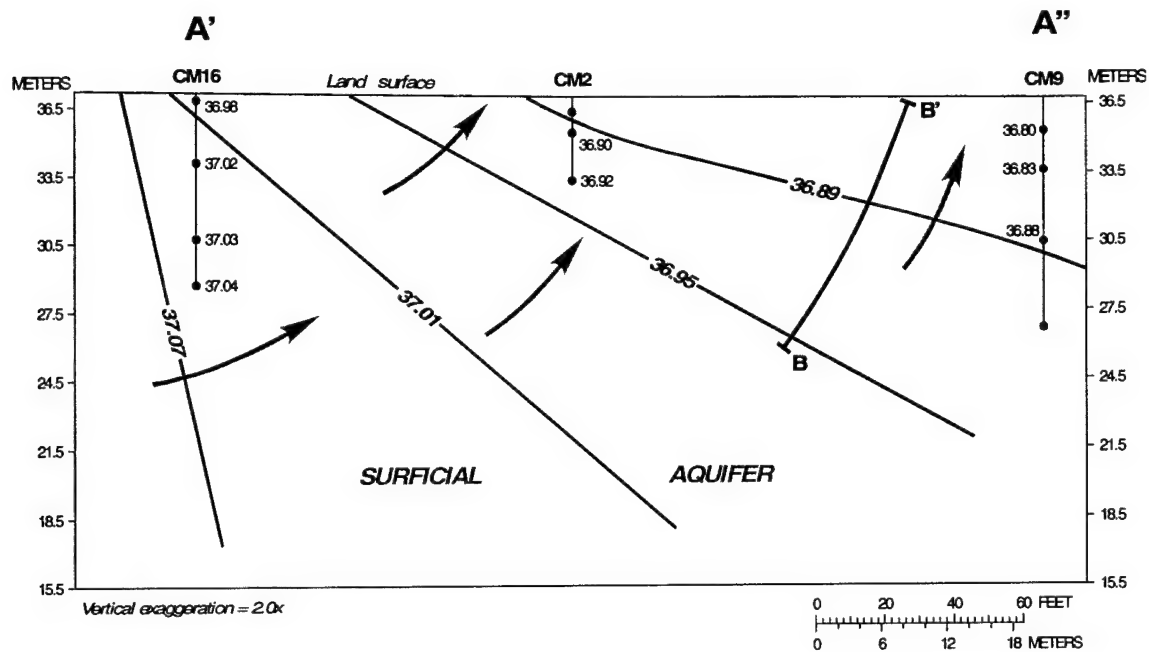
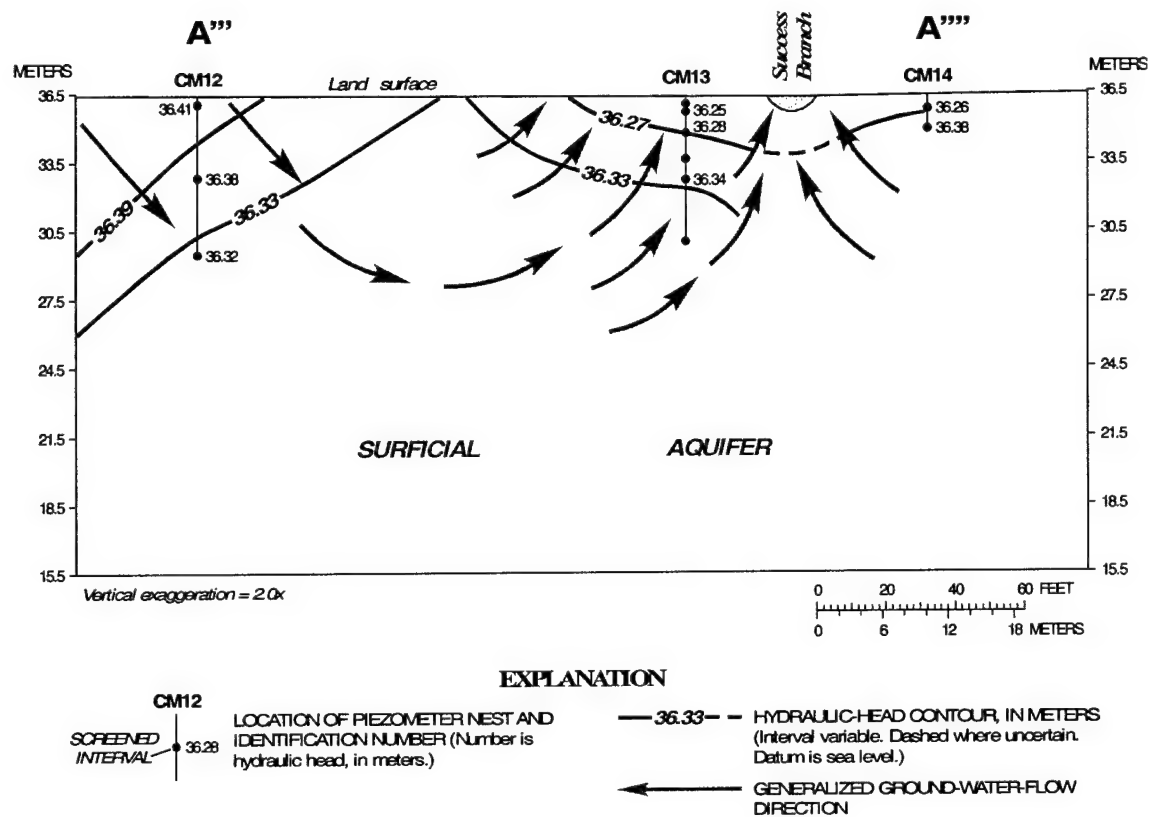


Figure 2.10. Cross-section through study area showing location of sediment core collection and local geology. The peat unit overlying the sand aquifer (Cohansey and Kirkwood Formations) is 0.30- to 1.2-m thick.



**Figure 2.11a.** Head distributions and ground-water-flow directions along sections A'-A'' and A'''-A'''' in the Colliers Mills Wildlife Management Area wetland site on September 12, 2000. (Refer to figure 2.5 for line of section A-A''''.)

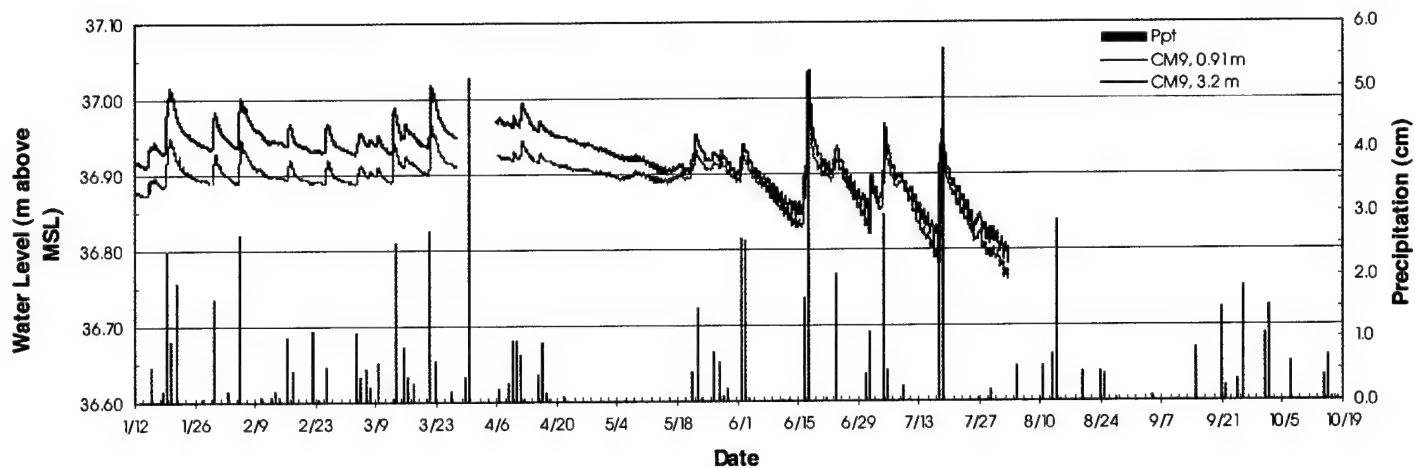




**Figure 2.11b.** Head distributions and ground-water-flow directions along section A'''-A'''' in the Colliers Mills Wildlife Management Area wetland site on March 27, 2001. (Refer to figure 2.5 for line of section A-A''''.)

(a)

CM9 Wells---Jan. 12 through Oct. 18, 2001



(b)

CM13 Wells---Jan. 12 through Oct. 18, 2001

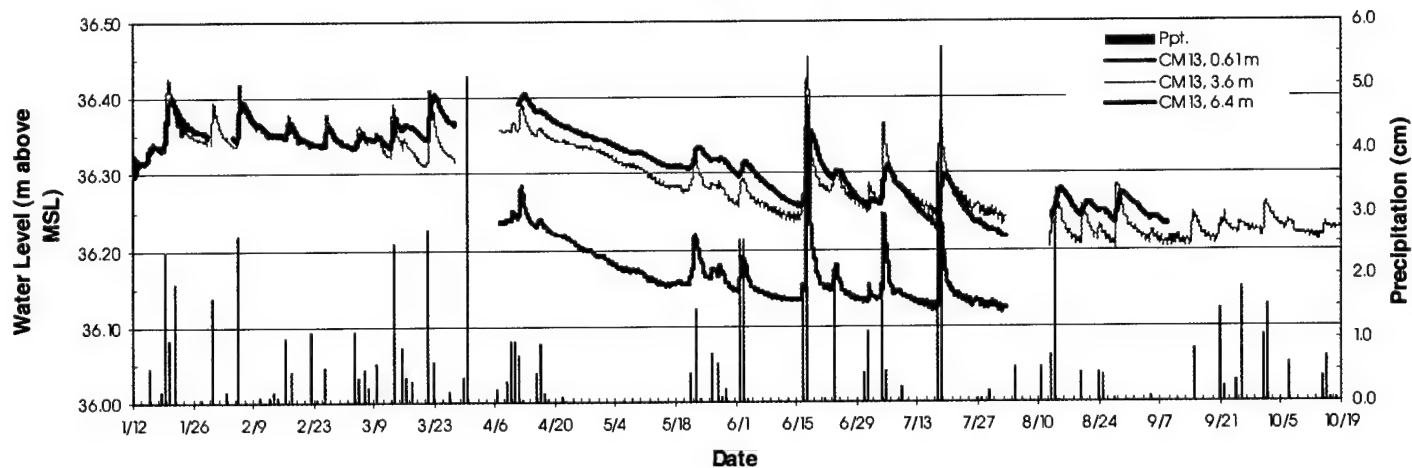
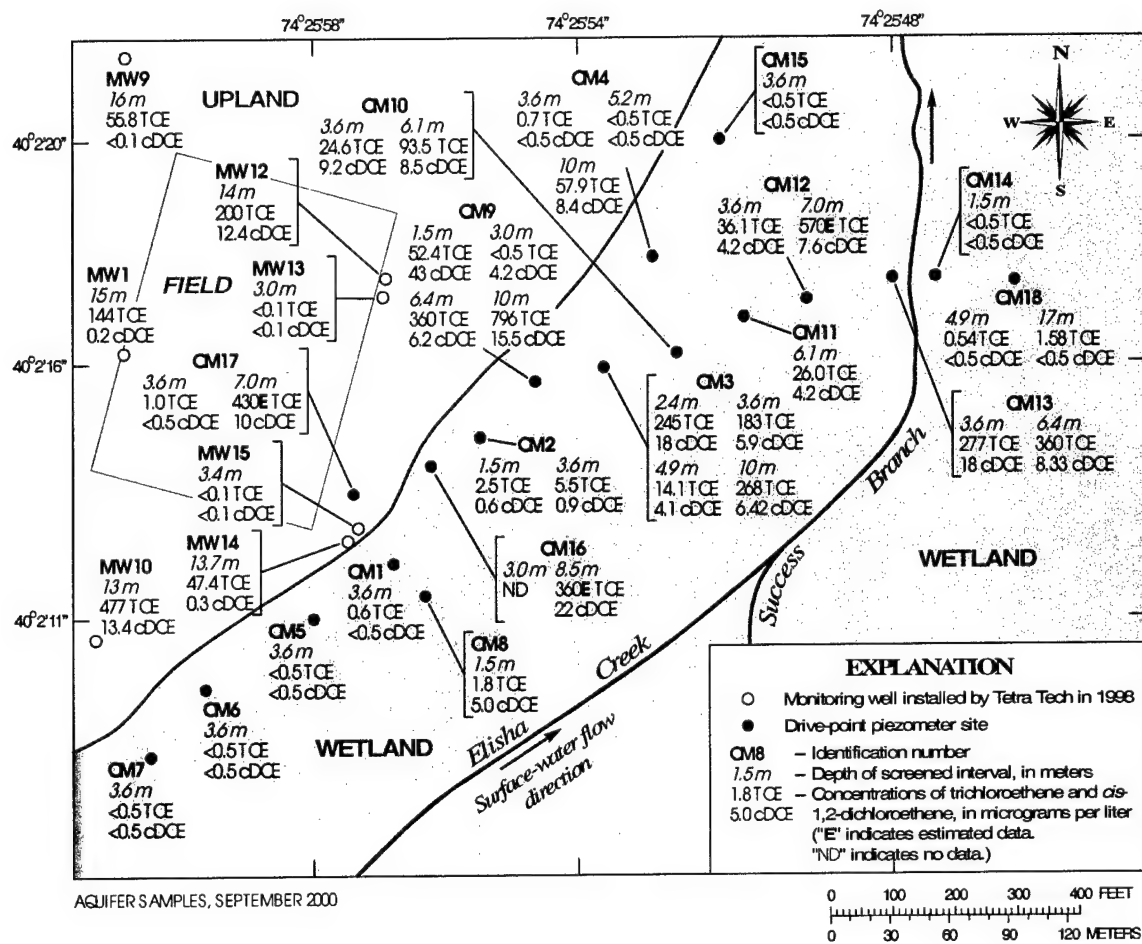


Figure 2.12. Hydrographs of continuous water-level measurements at sites (a) CM-9 and (b) CM-13 for approximately 10 months in 2001. [Breaks in water-level data in late March and early August represent disruptions in pressure transducer monitoring when sampling and/or slug tests were performed.]



**Figure 2.13.** Concentrations of trichloroethene (TCE) and *cis*-1,2-dichloroethene (cDCE) in piezometer samples from the aquifer at the ESTCP demonstration area at BOMARC Missile Facility / Colliers Mills Wildlife Management Area wetland site, September 2000.

[Data shown for the new CM piezometers installed in 2001 are from the March 2001 sampling event. Data shown for MW wells (previously installed by TetraTech) are from USGS personnel in Trenton, NJ, May 2000. Screen depth noted is the depth in meters below ground surface to the bottom of the screened interval (0.15 m screened interval in all CM piezometers).]



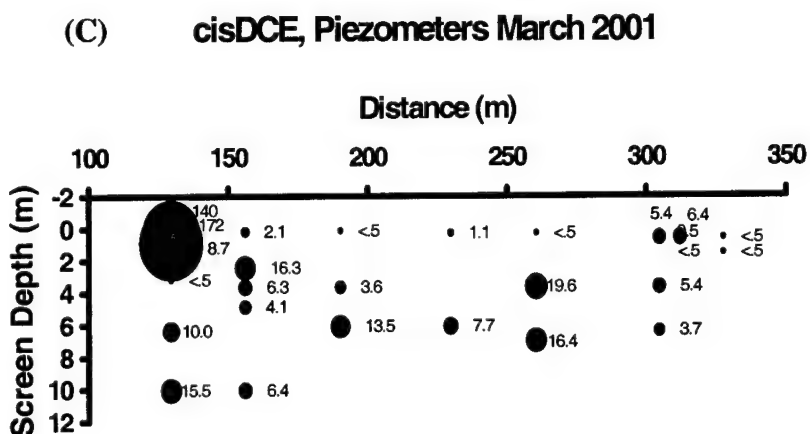
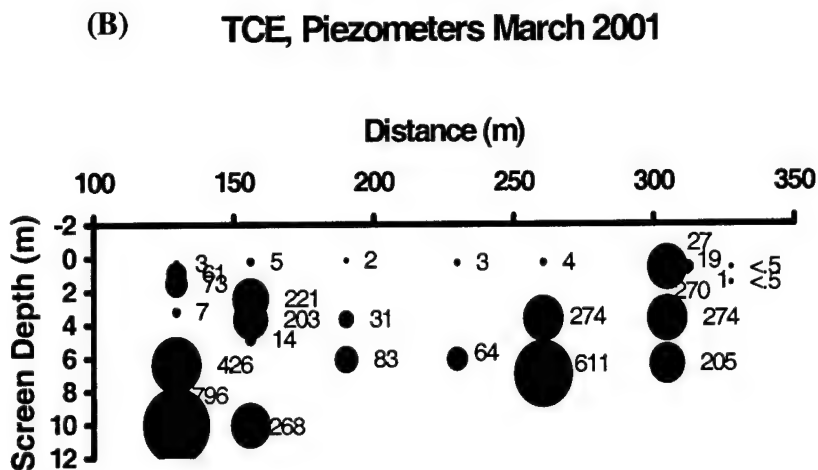
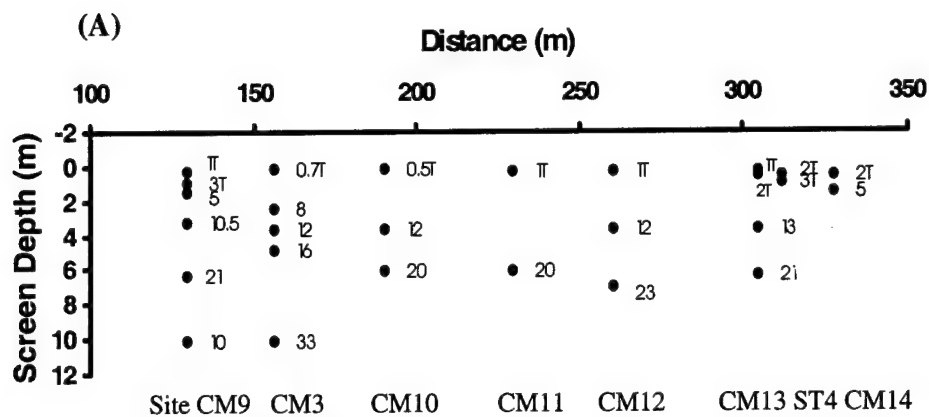


Figure 2.15. (A) Location of screened intervals, (B) TCE concentrations, and (C) cis DCE concentrations for piezometers located along a transect from the wetland boundary at site CM9 to the stream (between sites CM13 and CM14), March 2001.

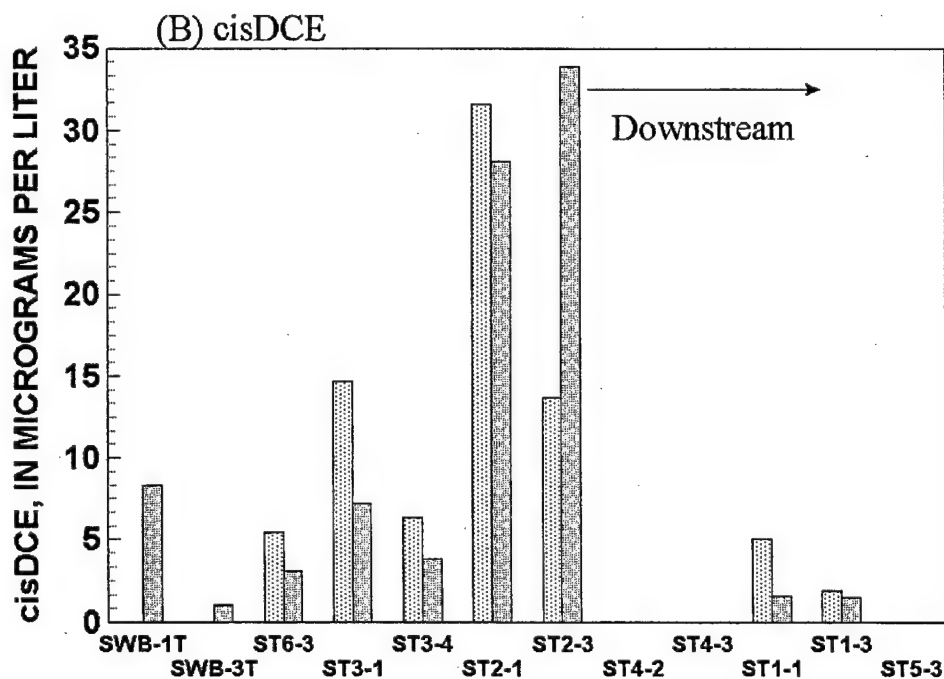
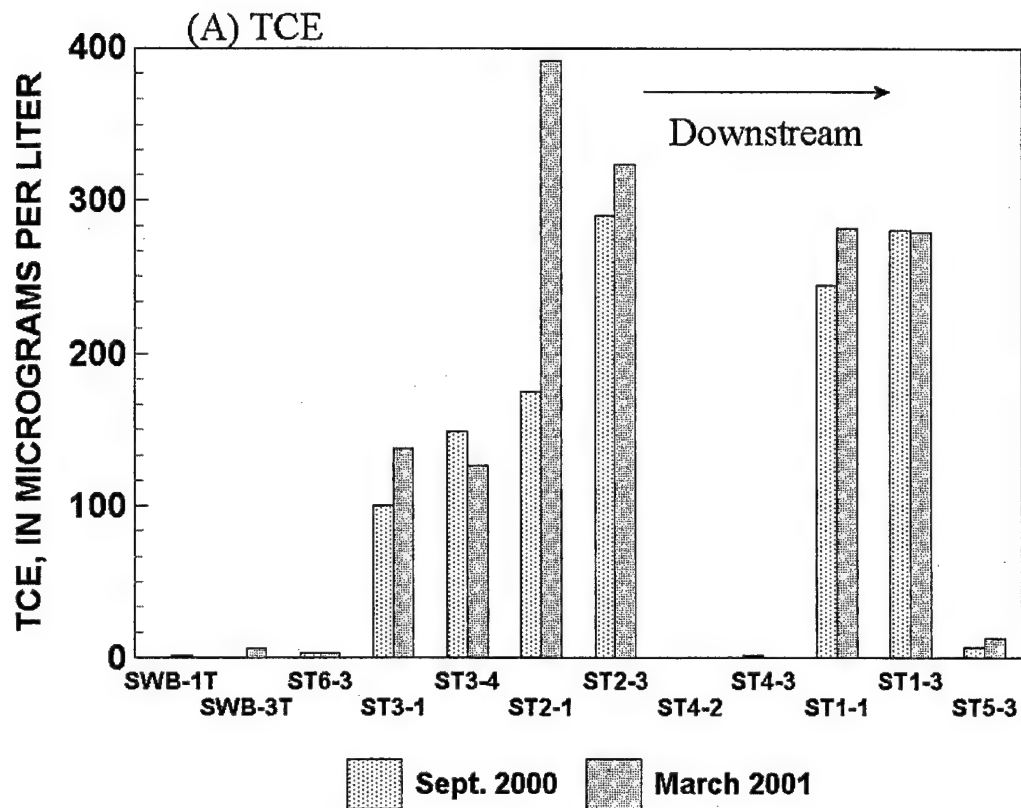


Figure 2.16. Concentrations of (A) TCE and (B) cisDCE in ground water collected from streambed piezometers in September 2000 and March 2001. Streambed piezometer site ST4 is adjacent to piezometer sites CM13 and CM14 on the streambanks.

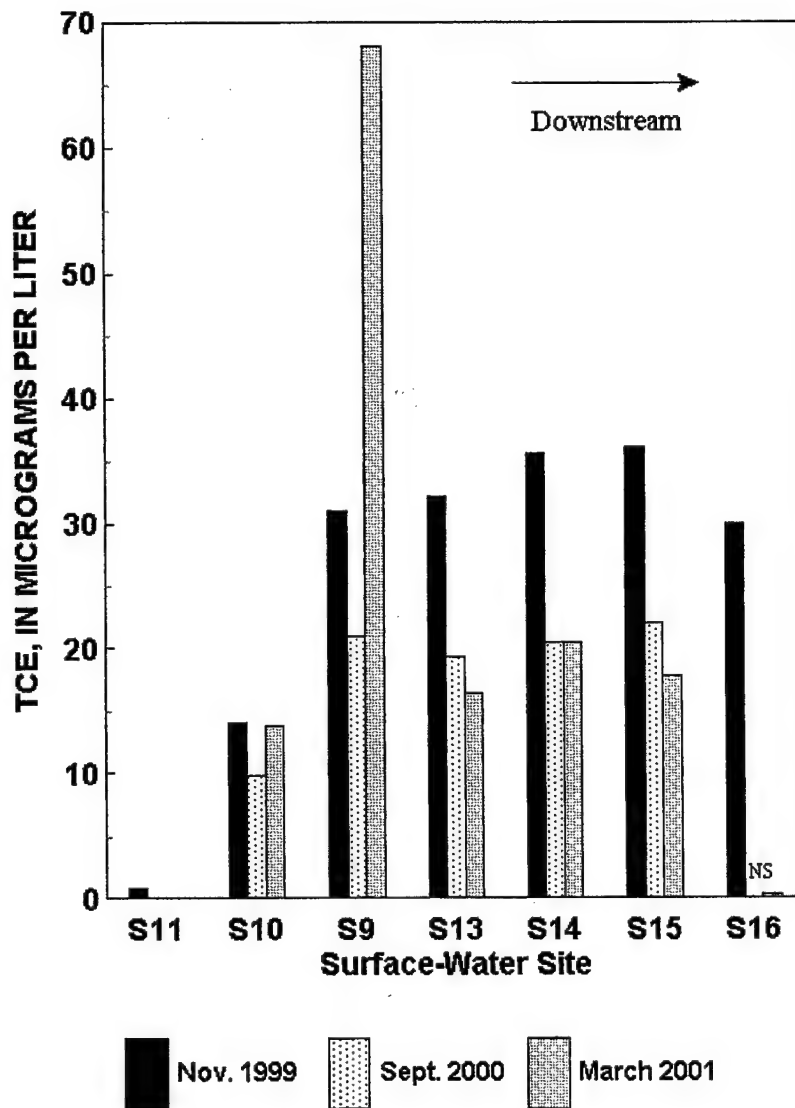


Figure 2.17. Concentrations of TCE in surface-water samples. Surface-water site S13 is adjacent to piezometer site ST4 in the streambed and piezometer sites CM13 and CM14 on streambanks. ["NS" indicates not sampled.]



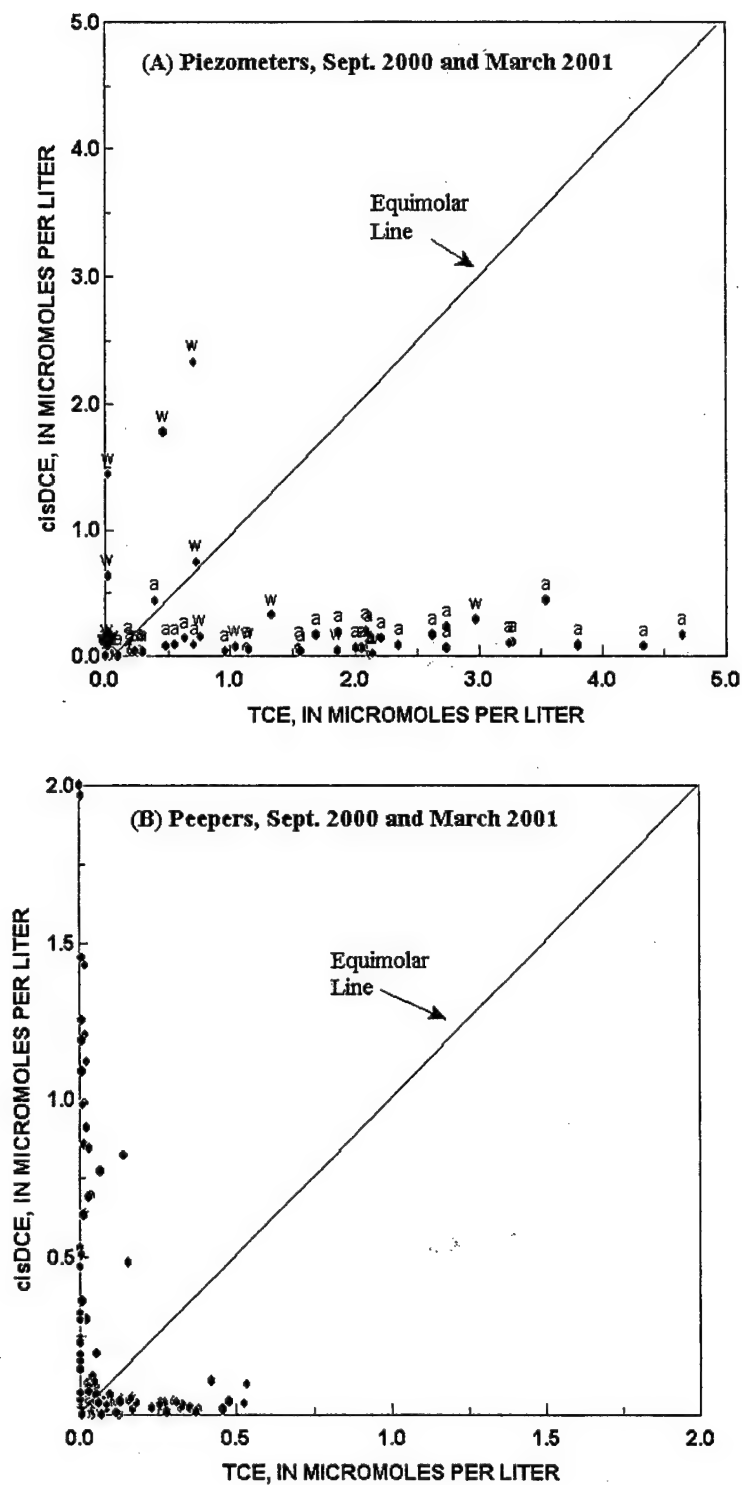


Figure 2.18. Molar concentrations of cisDCE compared to TCE in (A) piezometer samples and (B) peeper samples. [A "w" indicates a sample from a piezometer screened in the wetland sediment, and "a" indicates aquifer samples in (A). All peeper samples are from wetland or stream-bottom sediments.]

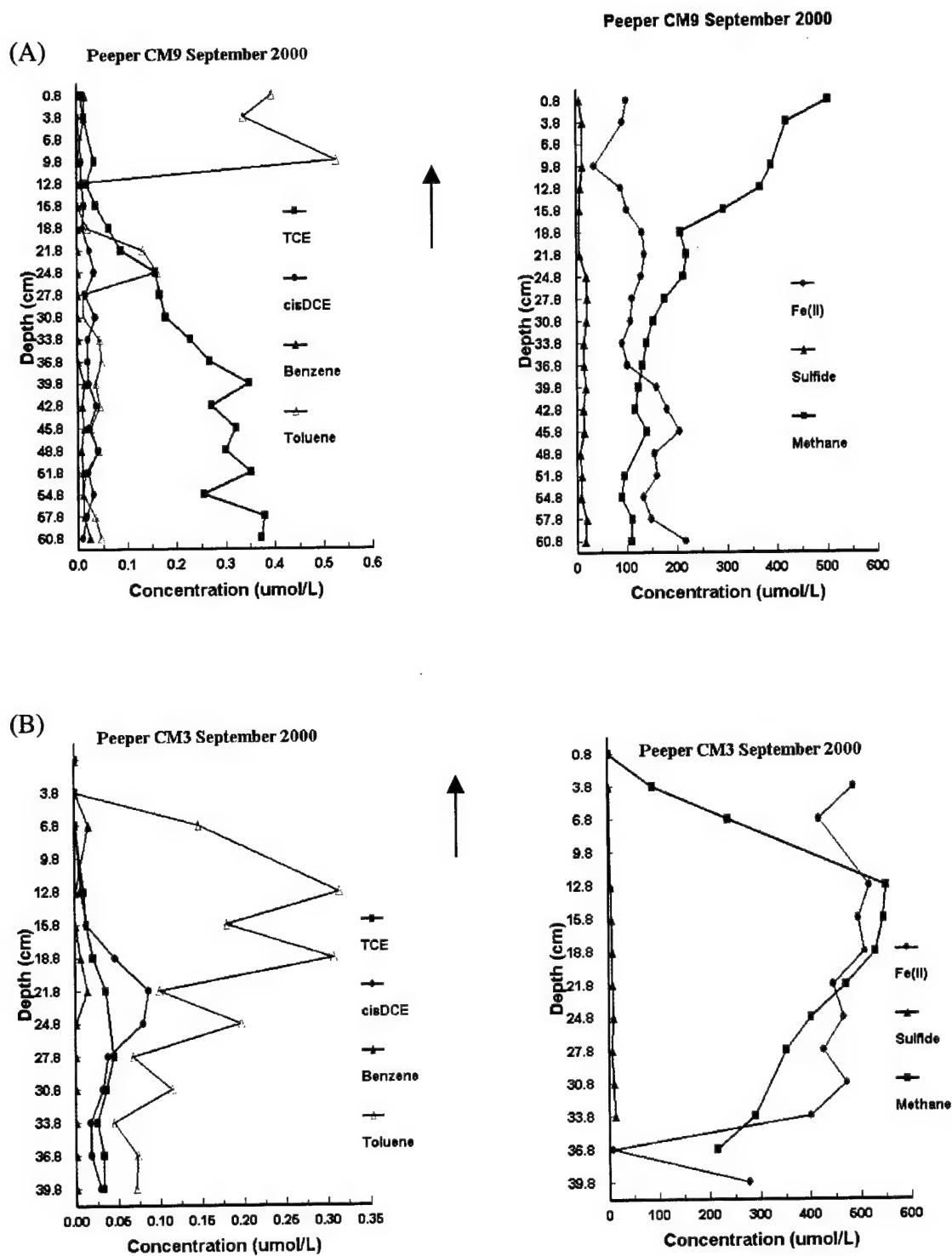


Figure 2.19a, b. Concentrations of volatile organic compounds and redox constituents in peepers at sites (A) CM9 and (B) CM3 in September 2000. Arrows indicate groundwater-flow direction.

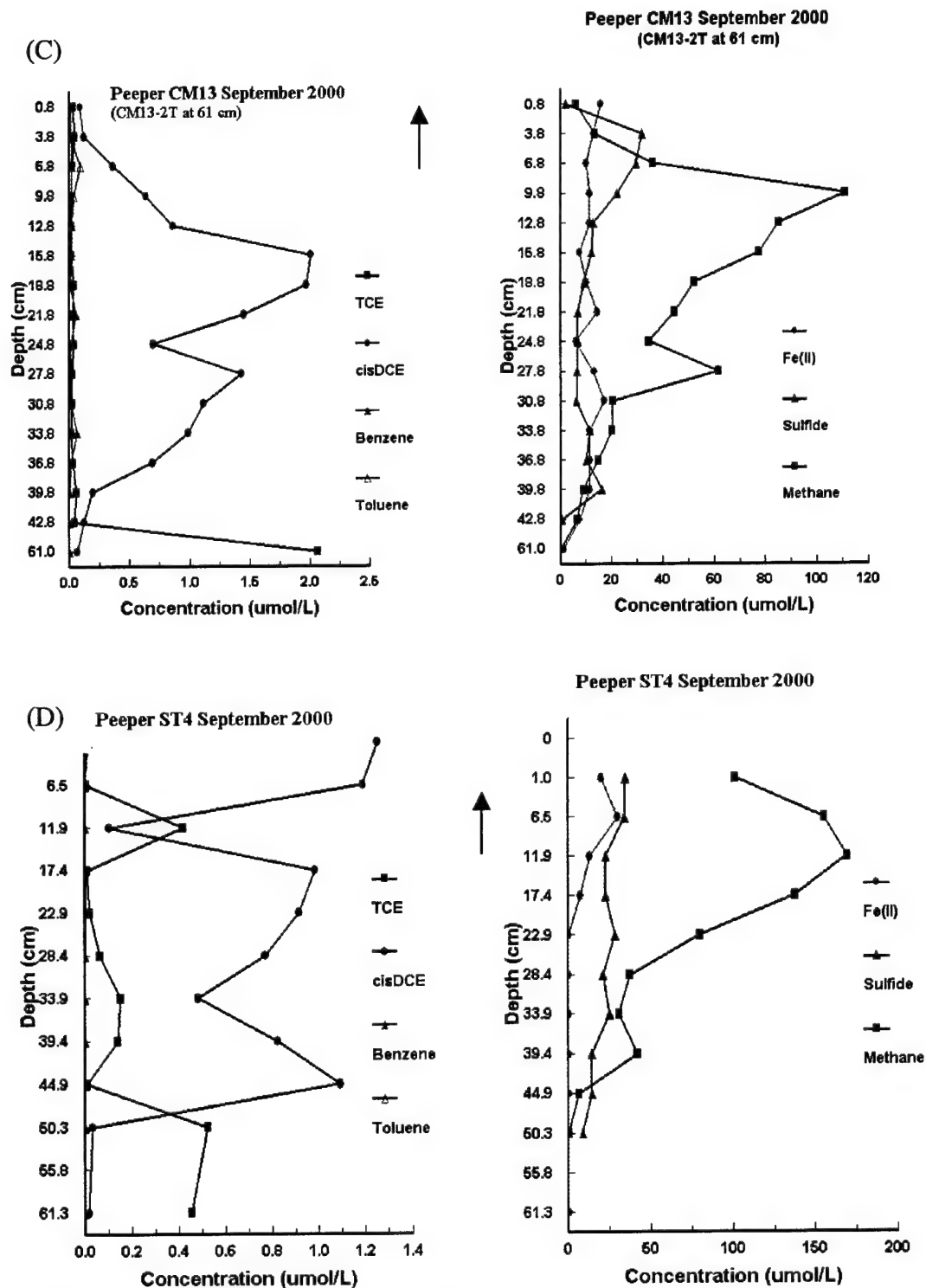


Figure 2.19c,d. Concentrations of volatile organic compounds and redox constituents in peepers at sites (C) CM13 and (D) ST4 in September 2000. Arrows indicate ground-water-flow directions.

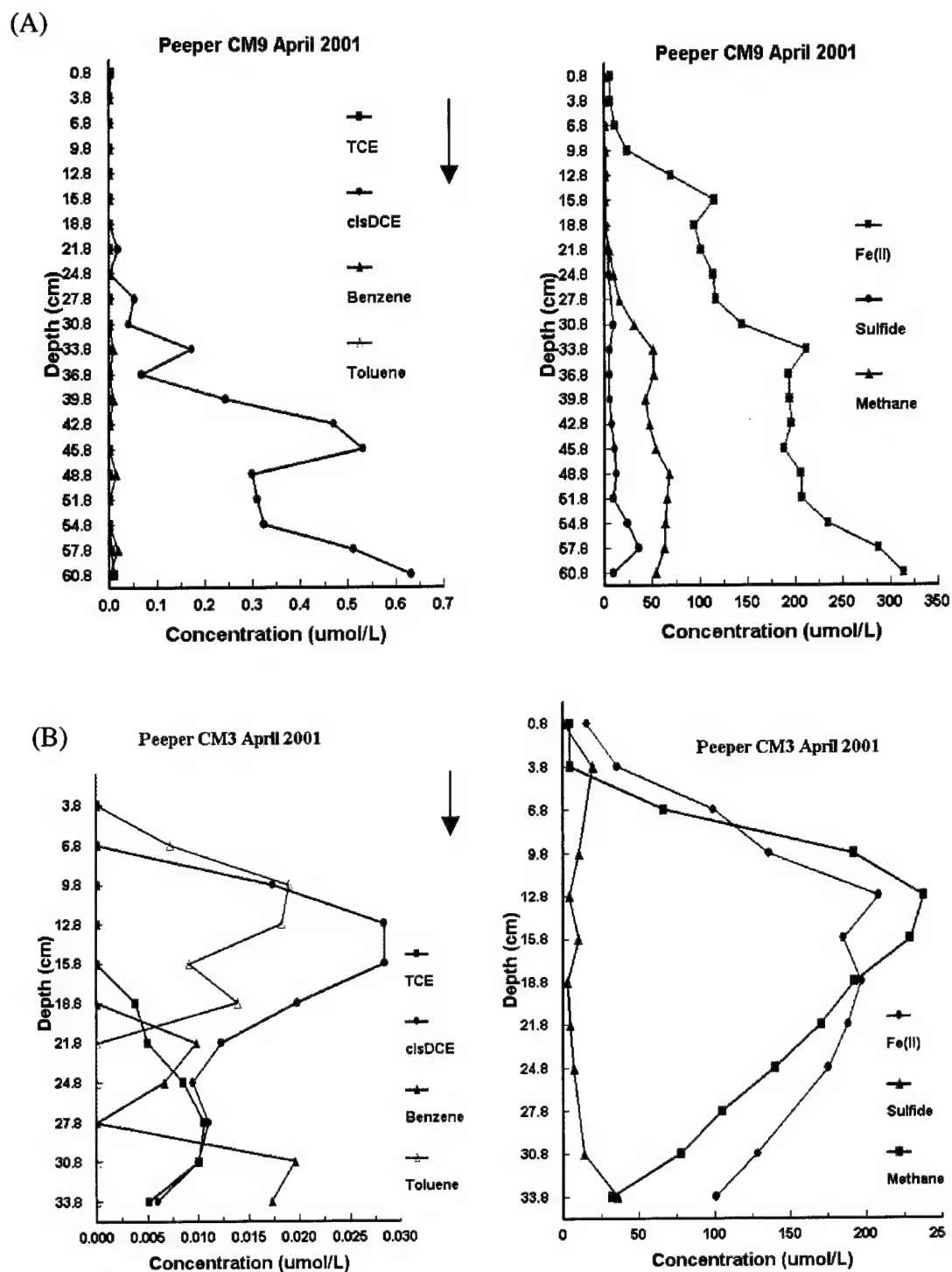
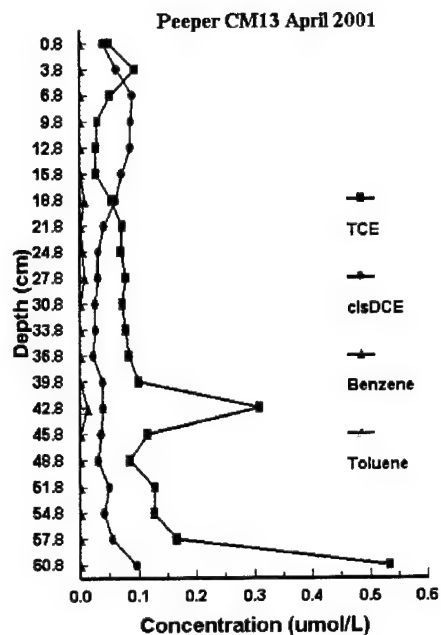
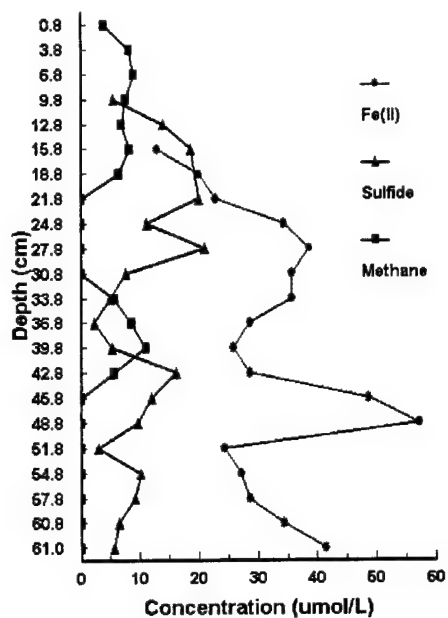


Figure 2.20a,b. Concentrations of volatile organic compounds and redox constituents in peepers at sites (A) CM3 and (B) CM9 in March 2001. Arrows indicate ground-water-flow directions.

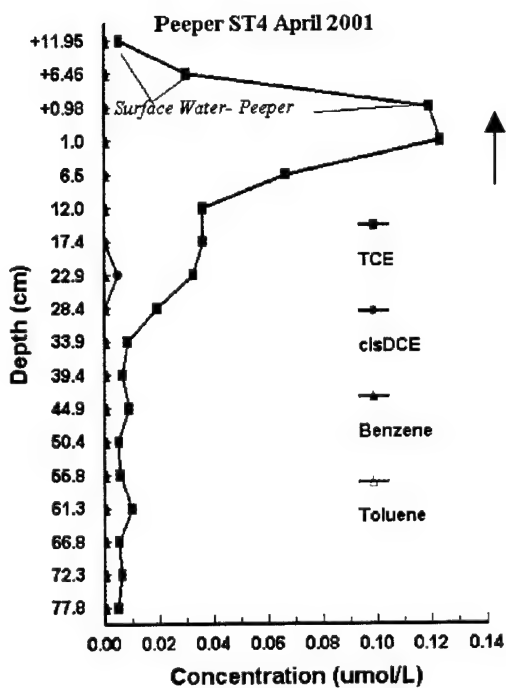
(C)



Peeper CM13 April 2001



(D)



Peeper ST4 April 2001

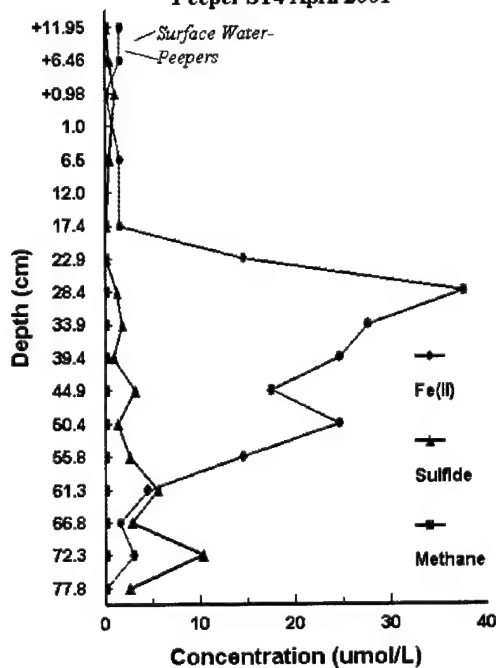


Figure 2.20c,d. Concentrations of volatile organic compounds and redox constituents in peepers at sites (C) CM13 and (D) ST4 in March 2001. Arrows indicate ground-water-flow directions.

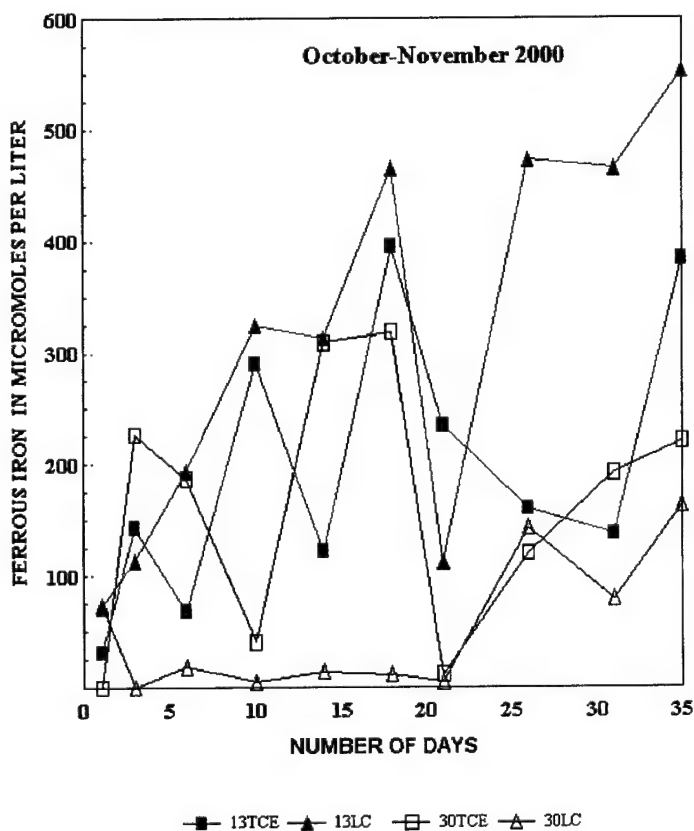
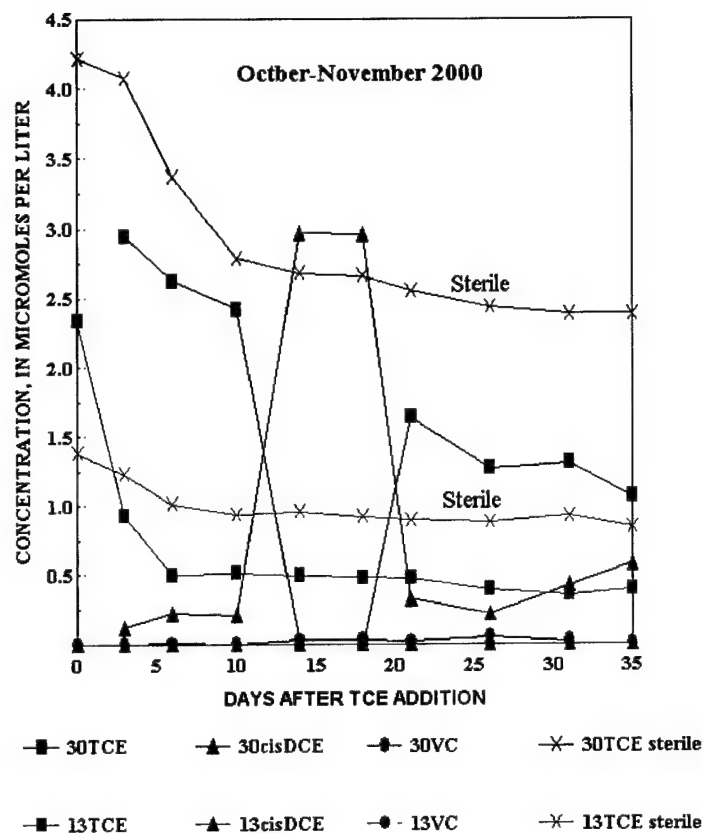


Figure 2.21. Concentrations of (A) TCE and the anaerobic daughter products cisDCE and VC and (B) ferrous iron in TCE-amended microcosms constructed with wetland sediment from site CM13 (indicated by "13" in the data label) at the Colliers Mills study area, New Jersey, or with wetland sediment from site WB30 (indicated by "30" in the data label) at the Aberdeen Proving Ground study area, Maryland, October-November 2000. The Colliers Mills microcosms are shown in red. Only TCE concentrations are shown for the sterile controls because cisDCE or VC was not detected. All data points represent the average of measurements in duplicate microcosms at each time point. In (B), "LC" in the treatment name indicates live controls that were not amended with TCE.

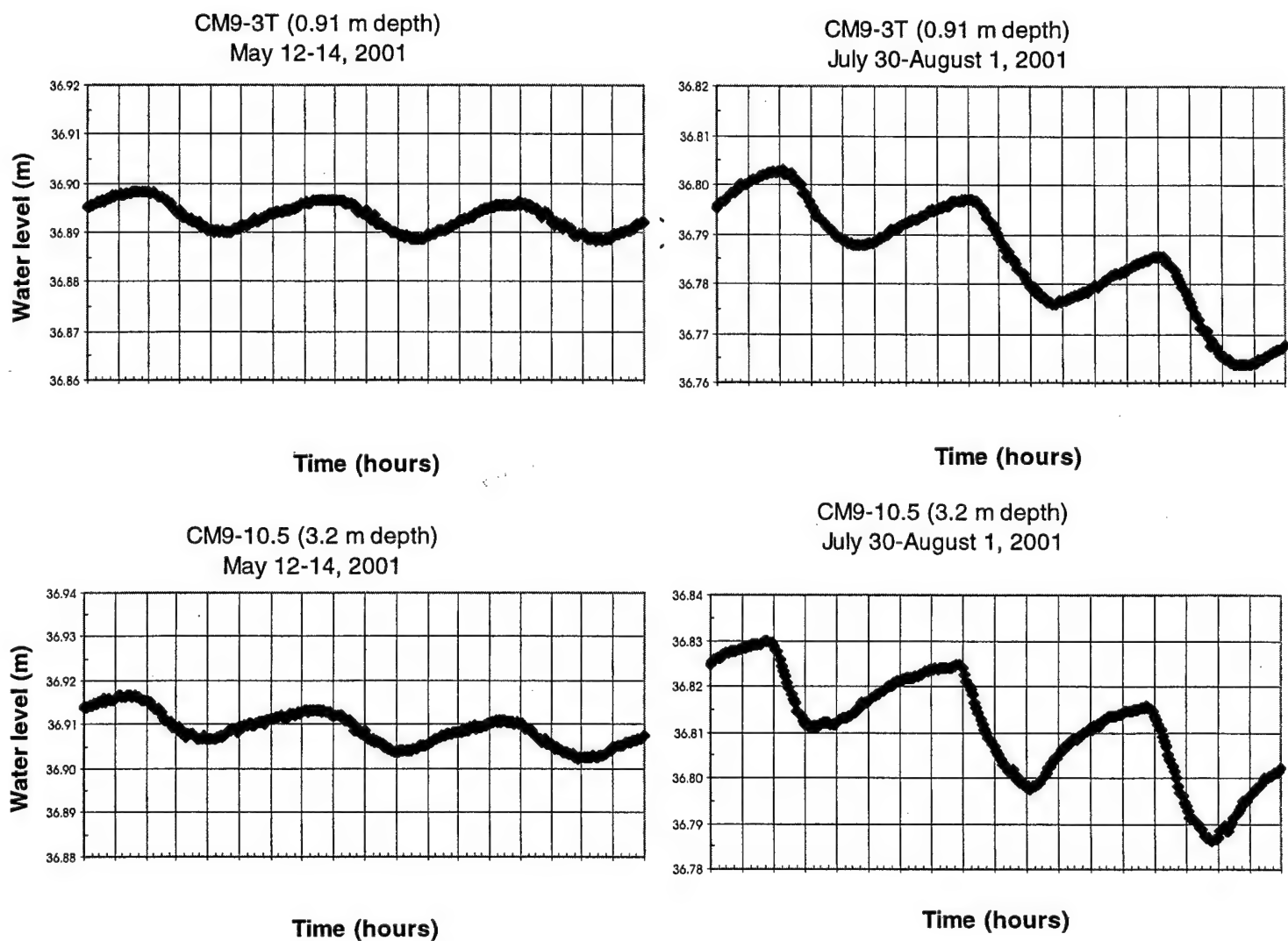
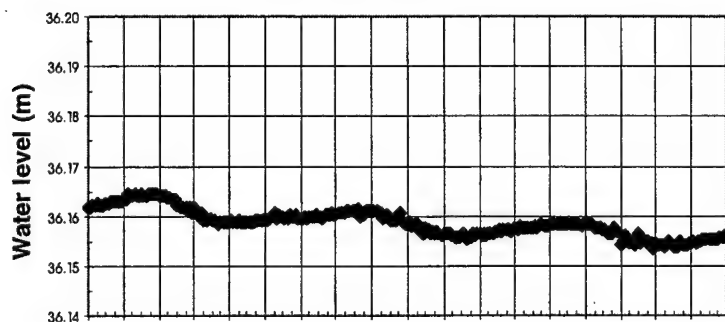


Figure 2.22. Diurnal water-level fluctuations, in meters above mean sea level, in 0.91 m and 3.2-m-deep piezometers at site CM9 before (May 2001) and during peak vegetation activity (July-August 2001).

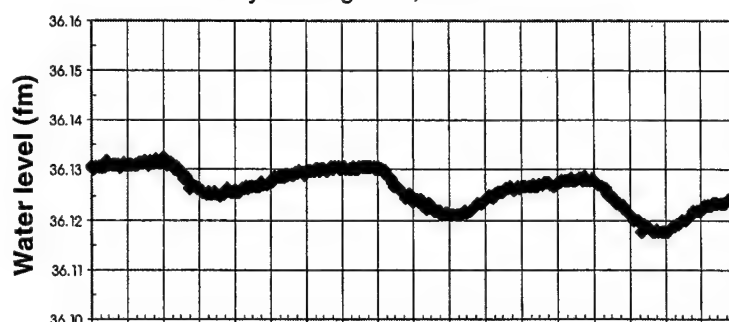


CM13 (0.61 m depth)  
May 12-14, 2001



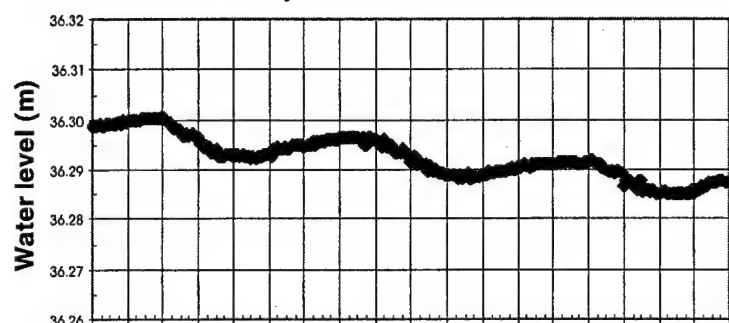
Time (hr)

CM13 (0.61 m depth)  
July 30-August 1, 2001



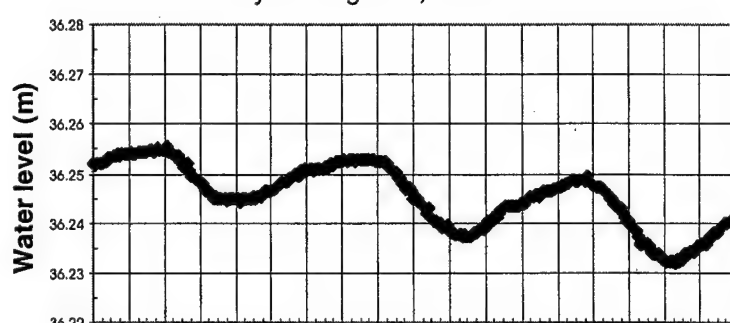
Time (hr)

CM13 (3.6 m depth)  
May 12-14, 2001



Time (hr)

CM13 (3.6 m depth)  
July 30-August 1, 2001



Time (hr)

Figure 2.23. Diurnal water-level fluctuations, in meters above mean sea level, in 0.61 m and 3.6-m-deep piezometers at site CM13 before (May 2001) and during peak vegetation activity (July-August 2001).

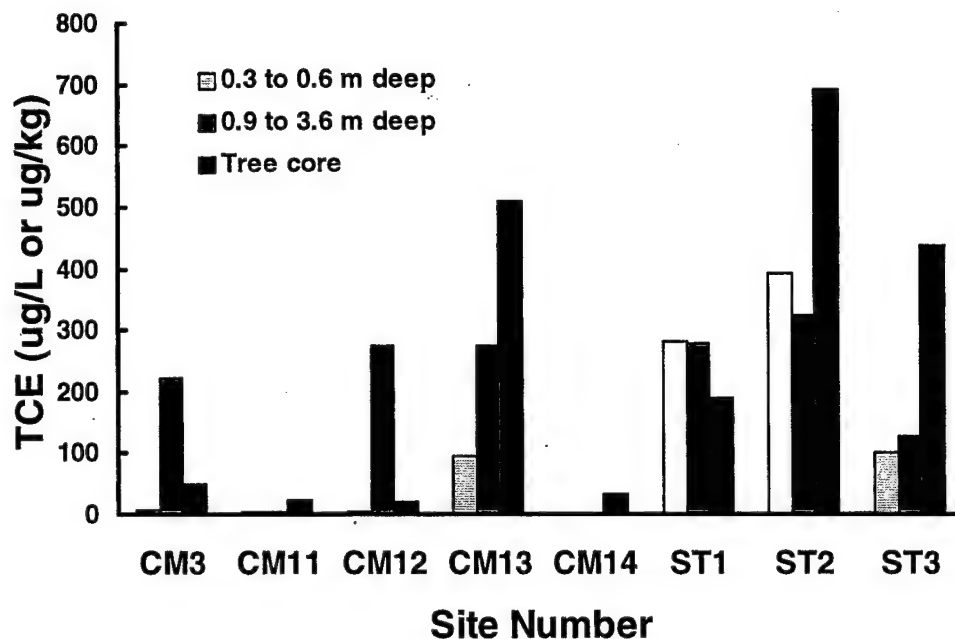


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# Section 3. Comparison of Porewater Sampling Methods and Evaluation of a Voltammetric Microelectrode to Characterize Natural Attenuation in Wetlands

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# **Section 3. Comparison of Porewater Sampling Methods and Evaluation of a Voltammetric Microelectrode to Characterize Natural Attenuation in Wetlands**

## **3.1 Introduction**

Wetlands require special considerations for sampling methodologies because of the largely vertical ground-water flow directions, the small flow rates and slow recoveries that often are observed in wells, the extremely small scales over which great changes in biogeochemical reactions can occur, and the inability to use heavy equipment. Thus, determining the fate of contaminants in wetland ground water requires the collection of samples at discrete, closely spaced depth intervals with devices that can be installed and sampled with light and portable equipment. The West Branch Canal Creek wetlands at APG was chosen as the test site for different sampling devices used to collect data needed to evaluate natural attenuation of chlorinated solvents by wetland sediments. Piezometer transects already were in place and natural attenuation had been demonstrated at the APG wetland site before the start of this ESTCP project (see Section 1), providing a useful benchmark for determining placement of new sampling devices and for comparing the results of the methodologies examined in the present study (Figure 3.1). As part of this ESTCP demonstration, wetland porewater concentrations of volatile organic compounds (VOCs) and of 3 constituents critical to defining redox conditions-- iron, sulfide, and methane-- were compared using four different samplers placed at comparable depths. Water level-data also were collected and compared. An additional experiment was performed to determine the extent of local spatial heterogeneities in concentrations inherently present in the wetland sediments, independent of the sampling device used. An examination of the costs and logistical considerations for each method, such as the ease of installation of the sampling devices, also are presented.

In addition to testing different methods to collect samples, a different method to analyze samples for redox constituents was tested. Electrochemical techniques using voltammetric microelectrodes were used to determine redox-sensitive species in collected water samples and by *in situ* measurements. A gold amalgam (Au/Hg) voltammetric microelectrode system (Model DLK-100 Electrochemical Analyzer) is a promising new technique to measure *in situ* concentrations of several major redox species and metals simultaneously at millimeter- and centimeter-depth intervals using a single working electrode (Brendel and Luther, 1995; Luther et al., 1998, 1999). The technology is capable of determining dissolved oxygen, iron, manganese, and sulfur species as well as other metals. Although a number of analyte-specific membrane microelectrodes, including oxygen, hydrogen sulfide, pH, and carbon dioxide, have been used to determine concentration profiles of single species in sediments since the early 1980's, a tool to simultaneously measure concentration gradients of several key redox species in sediments was not available until recently (Brendel and Luther, 1995; Luther et al., 1998, 1999). To determine

different species by repeated *in situ* measurements, voltammetric analyses are performed over a wide potential range, using a conditioning step between each potential scan to restore the electrode surface without removing the microelectrode from the sediment (Luther et al., 1999). Several major advantages of this microelectrode technique make it an especially promising tool for studying contaminant fate and ground-water/surface-water interactions in wetlands and stream-bottom sediments, including the ability to obtain (1) *in situ* measurements of porewater concentrations without removing sediment or water samples and, therefore, with minimum disturbance of natural conditions at the site, (2) instantaneous measurements in the field, (3) highly detailed depth profiles, and (4) concentrations of multiple species nearly simultaneously. In addition, the equipment is easily portable. Environmental testing and application of this type of microelectrode technology is limited, although the electrochemical theory is well developed and has been used in many other applications (Brendel and Luther, 1995). The limited *in situ* environmental testing that has been published has focused on sub-millimeter depth resolution of the upper 50 mm or less of marine sediments and in sediment cores from a salt marsh (Brendel and Luther, 1995; Luther et al., 1998, 1999). Because of the potential advantages of this electrochemical technique for defining redox conditions in wetland sediments, the technology was tested as part of this ESTCP demonstration.

Other methods of collecting data required to characterize natural attenuation originally were planned to be tested as part of this ESTCP demonstration but were rejected after preliminary tests or information gathering. Use of the Waterloo Profiler, which is a direct push ground-water sampling tool that is designed to collect multiple depth-discrete samples in a single hole, was tested during installation of the additional sampling devices at APG. Although this technology allows for rapid delineation of the vertical distribution of contaminants in sand aquifers, the low hydraulic conductivity of the APG wetland sediments made it difficult to obtain samples. Similarly, wetland sediment from the APG site was used to construct column tests to determine biodegradation rates and controlling factors in a flow-through system. The laboratory column studies, conducted by Dr. Eric Weber, U.S. Environmental Protection Agency, were designed to simulate the movement of chlorinated solvents from the aerobic zone of the aquifer to the highly reducing zones of the wetland sediment. Slow flow rates and clogging of sampling ports by fine-grained silt, however, caused the termination of these experiments. Similarly, the use of *in situ* microcosms, developed by the University of Waterloo (Gilham et al., 1990), and of forced gradient tracer tests were considered for determining *in situ* degradation and flow rates, respectively, but were rejected because of the low hydraulic conductivity of the wetland sediments. Results for the sampling and analytical methods that were tested were used in development of a protocol addendum for the assessment of natural attenuation of chlorinated solvent plumes discharging into wetlands (see Section 4 of this report).

### **3.2. Materials and Methods**

Wetland porewater concentrations of VOCs, iron, sulfide and methane were measured in March and June 2000 using four different sampling devices. These devices included: (1) 1.9-cm-diameter, stainless-steel drive-point piezometers with 15-cm-long screened intervals, (2) multi-level polyethylene samplers (MLSs) that contain seven 7.6-cm-long screened depth intervals in one borehole, (3) 0.64-cm-diameter, stainless-steel tube samplers that have inverted screens at the bottom, and (4) 60-cm-long and 120-cm-long acrylic porous-membrane diffusion samplers (peepers) with 21 and 22 rows of sampling chambers, respectively. All four sampling



devices were installed within a 1-m radius of each other at comparable depths at the WB34 and WB36 sites, and all devices except the peepers were installed at the WB23, WB24, WB26, and WB30 sites (Table 3.1; Figure 3.1). The sampling devices mostly were screened in the upper peat unit or lower clayey unit of the wetland sediments, but some of the drive-point piezometers and MLSs were screened near the top of the aquifer (Table 3.1). The four sampling devices and methods used to collect water samples are described below and have been previously described in Spencer et al. (2000) and Dyer et al. (2002). Analytical methods were the same as described in Section 2.2.3.

**Table 3.1. Screen depths and lithologic units for the devices installed at 6 sites for sampling method comparisons. Peepers also were installed at sites WB34 and WB36.**

[Screen lengths are 15.2 cm for piezometers and 7.6 cm for multi-level samplers; tube samplers have inverted screens so that sample enters only at bottom of tube. Lithologic units: UP and LC, upper peat and lower clayey units of the wetland sediments, respectively; AQ, sand aquifer]

Piezometer name	Midpoint screen depth (cm)	Multi-level sampler name	Midpoint screen depth (cm)	Tube name	Screen depth (cm)	Lithologic unit
WB23A	22.9	WBM23A	22.9	WBT23A	22.9	UP
--	--	WBM23B	45.7	WBT23B	45.7	UP
WB23B	74.7	WBM23C	76.2	WBT23C	76.2	LC
--	--	WBM23D	152.4	WBT23D	152.4	LC
WB23C	266.7	WBM23E	266.7	WBT23E	266.7	LC
--	--	WBM23F	327.7	--	--	LC
WB23D	388.6	WBM23G	388.6	--	--	AQ
WB24A	35.1	WBM24A	36.6	WBT24A	36.6	UP
--	--	WBM24B	67.1	WBT24B	67.1	UP
WB24B	99.1	WBM24C	100.6	WBT24C	100.6	UP
--	--	WBM24D	182.9	WBT24D	182.9	UP
--	--	WBM24E	243.8	--	--	LC
--	--	WBM24F	365.8	--	--	AQ
WB24E	510.5	WBM24G	512.1	--	--	AQ
WB26A	38.1	WBM26A	39.6	WBT26A	39.6	UP
WB26B	83.8	WBM26B	82.3	WBT26B	82.3	UP
WB26C	129.5	WBM26C	131.1	WBT26C	131.1	UP
WB26D	175.3	WBM26D	173.7	WBT26D	173.7	UP
--	--	WBM26E	219.5	WBT26E	219.5	LC
WB26E	275.8	WBM26F	274.3	--	--	LC
WB26F	464.8	WBM26G	466.3	--	--	AQ
WB30A	35.1	WBM30A	35.1	WBT30A	35.1	UP
WB30B	68.6	WBM30B	68.6	WBT30B	68.6	LC
--	--	WBM30C	99.1	WBT30C	99.1	LC
WB30C	144.8	WBM30D	144.8	WBT30D	144.8	LC
WB30D	205.7	WBM30E	205.7	WBT30E	205.7	LC
--	--	WBM30F	297.2	--	--	LC
WB30E	388.6	WBM30G	388.6	--	--	AQ
WB34A	53.3	WBM34A	53.3	WBT34A	53.3	UP
--	--	WBM34B	83.8	WBT34B	83.8	UP
--	--	WBM34C	114.3	WBT34C	114.3	UP
--	--	WBM34D	144.8	WBT34D	144.8	LC
--	--	WBM34E	175.3	WBT34E	175.3	AQ
--	--	WBM34F	201.2	--	--	AQ
WB34B	230.1	WBM34G	228.6	--	--	AQ
--	--	--	--	WBT36A	15.2	UP
--	--	WBM36A	30.5	WBT36B	30.5	UP
--	--	--	--	WBT36C	45.7	UP
WB36A	59.4	WBM36B	61.0	WBT36D	61.0	UP
WB36B	89.9	WBM36C	91.4	WBT36E	91.4	UP
--	--	WBM36D	121.9	WBT36F	121.9	UP
--	--	WBM36E	152.4	WBT36G	152.4	UP
--	--	WBM36F	182.9	WBT36H	182.9	AQ
WB36C	224.0	WBM36G	225.6	--	--	AQ

### 3.2.1 Drive-Point Piezometers

Drive-point piezometers from previous APG studies already were present at the wetland site before the ESTCP demonstration. Six of the drive-point piezometer clusters (2 to 6 drive points per cluster; 23 points total) were used for device comparison. These clusters are located at sites WB23, WB24, WB26, WB30, WB34, and WB36 (Figure 3.1). The 15-cm-long screened-interval depths range from 0.15 m to about 8.4 m below land surface; however, only those piezometers whose screened intervals are located in the wetland sediments and at the top of the aquifer were used for device comparison. Individual piezometers within each cluster are spaced less than 0.6 m apart at each site.

Drive-points used were Solinst Canada, Ltd.<sup>1</sup> ([www.solinst.com](http://www.solinst.com)) Model 615S shielded stainless-steel drive-points. A schematic of the Solinst 615S is shown in Figure 3.2. The shielded drive-point has a single-use shield to protect the filter inlets to the drive-point from smearing and plugging during installation. A 1.3-cm-diameter Teflon sampling tube was attached to the drive-point using the tubing barb at the top of the drive-point. Water samples contact only the stainless-steel drive-point and the Teflon inner sample tube. Drive-points were attached to lengths (1.6 to 2.3 m are common) of 1.9-cm steel drive pipe. Heavy-duty couplings (Solinst) were used to connect pipe lengths. Using a specially designed adaptor to protect the inner tubing, the piping was driven into the subsurface using either a slide bar hammer or vibratory power hammer. When the drive-point was at depth, the piping was pulled up 15 cm to allow the protective shield to separate from the drive-point sampling tip and expose the inlet holes. The strengthened connector at the top of the drive-point provides an annular seal to prevent contamination from higher levels in the hole.

The drive-point piezometers were purged and sampled using either a peristaltic pump or a gas-tight 60-ml syringe attached with a three-way stopcock to 1.3-cm-diameter Teflon tubing that was inserted into the piezometers with its end placed near the mid-point of the screened interval. Potentiometric head water-levels were measured using a steel tape.

### 3.2.2 Multi-Level Samplers

The Multi-Level Monitoring System (MLS) is a new sampling technology provided by Precision Sampling, Inc. (Richmond, California; [www.precisionsampling.com](http://www.precisionsampling.com)) (Einarson, 2001). This monitoring system was used to assess both piezometric pressure and water quality in as many as seven screened-depth intervals in one borehole. Prior to insertion of this monitoring device, sediment cores were obtained from the borehole during drilling operations. MLSs were installed adjacent to the existing drive-point piezometers at sites WB23, WB24, WB26, WB30, WB34, and WB36 in August 1999.

The MLS consists of a 4.3-cm OD multi-chambered polyethylene tubing with seven 1-cm-diameter internal channels (Figure 3.3). The multi-chambered tubing is available in lengths as long as several hundred feet, and the desired length is cut in the field. Several sample ports were drilled into the individual channels at each desired depth, creating 7.6-cm-long sampling intervals. A sealant was injected to seal the chamber below the lowest port at each sampling

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<sup>1</sup> The use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government.

interval. Stainless-steel screens were secured around the ports at each sampling interval and then bound with a sand pack. Bentonite seals were secured to the sampler between the sand packs to prevent channeling of ground water from one sampling interval to another. The central chamber became the deepest sample port. At the base, the surrounding six chambers were sealed with sealant and a stainless-steel screen was secured over the base. The MLS was then inserted into a single drive casing with a 1,300-lb direct-push drill rig mounted on a small hand truck. The casing was withdrawn, and the sediment was allowed to collapse around the borehole.

The MLS chambers were purged and sampled using either a peristaltic pump or a gas-tight 60-ml syringe attached with a three-way stopcock to 0.6-cm-diameter Teflon tubing that was inserted into the MLS chamber with its end placed near the sample port. Water levels were measured using a steel tape.

### **3.2.3 Tube Samplers**

Six nests of four to seven tube samplers (Figure 3.4) were manually pushed to depths comparable to the drive-point piezometers and MLSs in the wetland sediments at sites WB23, WB24, WB26, WB30, WB34, and WB36. Tube samplers were installed immediately prior to sampling in March 2000. The tube samplers were constructed of thick-walled 0.64-cm-diameter stainless-steel tubing. A conical 7.6-cm-long, 100-mesh stainless-steel screen was inserted tightly into one end of the tube, forming an inverted screen. To prevent clogging of the screen during insertion, organic-free deionized water was forced into the tube concurrent with its insertion. To ensure that the thin tubes were installed vertically from the surface and to prevent leaning or horizontal movement once in place, the tubes were inserted through holes that had been drilled into two small untreated plywood platforms, one atop the other. The platforms were anchored to a nearby PVC pipe.

Purging and sampling were done using a gas-tight 10-ml glass syringe with a three-way stopcock attached to 0.3-cm-diameter Teflon tubing with its end inserted just above the top of the inverted screen. Potentiometric head measurements were not determined in these sampling devices because of their small diameters.

### **3.2.4 Peepers**

Peepers are passive ground-water sampling devices that were originally designed by Hesslein (1976) for studying redox constituents in lake bottom sediments. Discrete water-quality samples are obtained by diffusion into a vertical section of individual sample chambers (Figure 3.5). A local plastics fabricating company machined 60-cm-long peepers (hereafter, short peepers) and a 120-cm-long peeper (hereafter, long peeper) to our specifications for use in this demonstration (Figure 3.5). Sample chambers are spaced 3.0 cm and 5.5 cm apart vertically in the short and long peeper, respectively. Short peepers were installed at sites WB34 and WB36, and the long peeper was installed only at site WB36.

The body of the peeper is constructed from a solid 2.5-cm-thick acrylic plate. Oval chambers were cut completely through the plate. Two thin acrylic sheets, termed "membrane support plates", were machined in a similar fashion and attached with nylon screws to either side of the thick plate. The membrane support plates held a 0.2- $\mu$ m permeable membrane (HT Tuffryn, Pell Corporation, Ann Arbor, Michigan) over each side of the open chambers. A handle was machined into the top of the plate and the bottom was tapered into a sharp blade for ease of

insertion into sediments. The short peeper contained 2 columns with 21 rows of sample chambers; the long peeper contains 2 columns with 22 rows of sample chambers. The two chambers at each depth allow for duplicates and sample spares in case of perforation of one membrane. Each sample chamber in the short and long peepers hold approximately 11 and 23 ml of water, respectively.

To prepare the peeper for insertion into the wetland sediments, one side of the thick acrylic plate was covered with porous membrane paper and fastened with a membrane support plate. The chambers were filled with deionized water before covering the other side with membrane paper and a membrane support plate. Once assembled, the unit was purged with nitrogen gas overnight to remove oxygen from the water within the sample chambers and from the device itself. The peepers were then manually pushed vertically downward into the wetland sediments, with the top two horizontal chambers buried just under the air/land-surface interface. After the peeper is put into the subsurface, dissolved organic and inorganic components in the surrounding porewater diffuse through the membrane into the peeper chamber. Equilibration with the porewater usually is accomplished within 2 to 3 weeks (Carignan, 1984). The peeper was then withdrawn from the sediment, and the water within the chambers was sampled immediately using a gas-tight 10-ml glass syringe that had a short tube attached to it. Sample transfer was made to the appropriate sample vials for subsequent laboratory analysis of VOCs and methane ( $\text{CH}_4$ ). Reagents for colorimetric bypyridine analysis of total dissolved iron and ferrous iron were added immediately in the field, and sulfide was analyzed immediately in the field using the CHEMetrics System 1000 kit (see Section 2.2.3). Complete sampling of one peeper required 50 to 60 minutes.

In addition to the March and June 2000 sampling of all the sampling devices, an experiment was performed in May 2001 at one site to determine the extent of local spatial heterogeneities inherently present in wetland sediments. This experiment was used to evaluate variabilities that could be expected regardless of the sampling device used. Three 60-cm-long peepers were inserted approximately 0.6 m apart into the wetland sediments at site WB36 so that one was adjacent to the drive-point piezometer nest, one adjacent to the tube sampler nest, and one adjacent to the multi-level sampler. After equilibration, they were pulled and immediately sampled for ferrous iron, sulfide, methane, and VOCs.

### 3.2.5 Voltammetric Microelectrode

Voltammetry was used to obtain dissolved oxygen, manganese ( $\text{Mn(II)}$ ), total hydrogen sulfide, and ferrous iron ( $\text{Fe(II)}$ ) concentrations by *in situ* measurements in shallow wetland sediments and by measurements in peepers that had been equilibrated in the wetland sediment and subsequently removed for sampling. A model DLK-100A electrochemical analyzer (Analytical Instrument Systems, Inc., Ringoes, New Jersey) was coupled to a 0.1-mm-diameter gold/mercury ( $\text{Au/Hg}$ ) amalgam microelectrode that was encased in 5-mm-diameter glass and sealed with epoxy (Figure 3.6). The electrochemical methods used are the same as developed by Brendel and Luther (1995) and Luther et al. (1998, 1999). [Students advised by Dr. Peter Jaffe, Princeton University, made the working microelectrodes that were used and conducted the electrochemical analyses.] Calibration curves for each compound to be analyzed were made in the laboratory before field work began. Measurements were made at sites WB35 and WB19 in August and September 2000. For *in situ* measurements in shallow wetland sediments, the microelectrode was pushed vertically downward through the sediment using a micromanipulator

to accurately measure depths. For analyses in peeper cells, the microelectrode was placed directly in the sample chambers after the peeper was removed from the sediment. At each depth in the sediment or in each peeper chamber, triplicate voltammetric measurements were made in about 3 minutes by scanning a voltage range from  $-0.1$  to  $-2.0$  volts (V) and electrochemically conditioning the electrode between scans. Water samples were collected simultaneously for standard chemical analyses of redox constituents using the methods detailed in Section 2.2.3.

### **3.3 Comparison of Porewater Sampling Methods**

In the freshwater tidal wetland at APG, trichloroethene (TCE) and 1,1,2,2-tetrachloroethane (PCA) are the major parent contaminants that are discharging upward from the aquifer. 1,1,2-trichloroethane (112TCA), 1,2-dichloroethane (12DCA), *cis*- and *trans*-1,2-dichloroethene (12DCE), and vinyl chloride (VC) are the predominant, persistent daughter products observed in the anaerobic wetland sediments (Lorah and Olsen, 1999a, b). The sum of the parent compounds, the sum of the daughter compounds, and the total concentrations of VOCs measured in the porewaters are used here to compare contaminant concentrations in the different devices, although differences were occasionally observed in the distribution of individual VOCs. The redox-sensitive constituents used for device comparison include methane, reduced iron, and sulfide. In some of the samples used for device comparison, only total iron [combined Fe(II) and Fe(III)] was analyzed, but previous sampling efforts have shown that ferric iron concentrations are insignificant in the anaerobic wetland porewater. Therefore, Fe(II) and total iron concentration were sometimes compared when Fe(II) data were lacking. Concentrations determined in March and June 2000 for device comparisons were reported in Spencer et al. (in press), along with other recent data collected at the West Branch Canal Creek wetland site.

#### **3.3.1 Distribution of Redox-Sensitive Constituents and Chlorinated Volatile Organic Compounds in Shallow Porewater in Peepers Compared to Other Sampling Devices**

Comparisons were made among all four sampling devices in the shallow wetland sediments at sites WB34 and WB36 to maximum depths of 60 cm and 120 cm, respectively (the depths to which the peepers reached at each site). Because the placement of MLS, piezometers, and tube samplers were located at a limited number of depths at both sites, there were only a few data points to compare to the peeper devices at these shallow wetland depths. The different screen sizes of the sampling devices should be considered when comparing these concentrations. Because the piezometers had the longest screens (15 cm), they could draw a greater mix of water compared to the smaller sample inlets of the peepers and tube samplers. At site WB34, the MLSs and short peepers generally showed the highest concentrations of redox-sensitive constituents compared to the other sampling devices (Figure 3.7). Iron concentrations measured in the piezometers were about the same as those measured in the peepers, but the piezometers generally had the lowest concentrations of methane and sulfide (Figure 3.7). The peepers also were the best overall indicators of porewater redox chemistry for shallow depths in the wetland sediments at site WB36 (Figure 3.8). Both long and short peepers generally had the highest concentrations of methane, iron, and sulfide, although the MLSs had methane concentrations comparable to those in the peeper samples (Figure 3.8). As at site WB34, the piezometers compared well with the peepers in iron concentrations, but showed very little, if any, methane and sulfide. The tube samplers showed low concentrations of the three redox-sensitive species.



The generally higher concentrations of most redox constituents in the peepers may be attributed partly to the lower chance of sample aeration and volatilization in the peepers because samples are passively collected into chambers filled with deionized water. The tube samplers and piezometers that were screened in the shallow wetland sediment often required long recovery times after purging (4 to 24 hrs), increasing the chance of loss of volatile constituents before sample collection. Because of the low water volume available after recovery in these shallow tube samplers and piezometers, several days were sometimes required to obtain all samples. In addition, tubing to collect sample had to be inserted through a narrow diameter water column, and water samples were pulled from depth in all sampling devices except the peepers. The MLSs generally did not require long recovery times, most likely because of the sand packs surrounding the screens. Concentrations of methane, which is the most volatile of the redox constituents sampled, compared best between the MLSs and the peepers (Figure 3.9). Fe(II), which is less susceptible to volatilization and oxidation than methane or sulfide, showed the best agreement among all the sampling devices (Figure 3.9).

In addition to higher concentrations of the redox-sensitive species, the peepers sometimes showed higher concentrations of daughter VOCs and total VOCs compared to the other devices (Figure 3.9, 3.10, and 3.11). It is evident that the more closely spaced intervals of the peepers allowed more precise delineation of contaminant degradation along upward ground-water flowpaths toward the wetland surface (Figures 3.10 and 3.11). Overall, however, the daughter VOCs and total VOCs showed better agreement among the different sampling devices than observed for methane or sulfide (Figures 3.9). The differences in VOC constituents that were observed suggest that the different sampling devices were drawing water from different pore sizes or reaction zones, rather than simply showing effects of aeration or oxidation during sampling. For example, only the parent compounds TCE and PCA (shown as sum parents in Figures 3.10a and 3.11a) were observed in the tube samplers, whereas the peeper samples consisted predominantly of the daughter compounds 12DCE and VC (shown as sum daughters in Figures 3.10b and 3.11b). This difference could result from the tube samplers collecting ground water that is flowing along preferential flowpaths (such as root channels), where there is less time for biodegradation to occur compared to the water collected by diffusion in the peepers. Because of the low ground-water-flow velocity (about 1 m/yr) in the wetland sediments at this site, diffusion is likely a major transport mechanism. The peepers also showed seasonal changes in VOC concentrations that were not distinct in the other sampling devices. Peeper data from 2000 showed higher concentrations of VOCs (all as daughter compounds) in the summer (Figure 3.10) than in the winter or early spring (Figure 3.11), which is consistent with seasonal patterns observed in peepers sampled in 1995-99 (Lorah et al., 2000). The higher summer VOC concentrations in the peepers are believed to result from a higher mass flux of parent VOCs to the wetland sediments during this time, in a delayed response to high recharge to the aquifer upgradient of the wetland in the spring (Lorah et al., 2000). Although higher concentrations of VOCs were not observed in the aquifer underlying the wetland sediment, higher heads caused a greater mass flux of parent VOCs in the summer. Subsequent biodegradation in the wetland sediments resulted in higher concentrations of daughter VOCs in the wetland porewater sampled by the peepers in the summer compared to the spring (Lorah et al., 2000) (Figures 3.10 and 3.11). A seasonal change in VOC concentrations was not distinct in the MLS, tube samplers, or piezometers (Figures 3.11 and 3.11). These sampling devices showed approximately constant concentrations in the summer and spring (Figures 3.10 and 3.11), again suggesting that these



sampling devices preferentially sample flow from larger pore spaces where biodegradation is limited.

### **3.3.2 Distribution of Redox-Sensitive Constituents and Chlorinated Volatile Organic Compounds in Deeper Porewater**

Over depth ranges greater than the peepers could reach (60 to 120 cm), concentrations of VOCs and redox-sensitive constituents often were relatively consistent between the tube samplers, MLSs, and drive-point piezometers. The MLS wells had the highest concentrations of methane when all three devices at similar depths were compared, whereas the piezometers generally showed the lowest concentrations (Figure 3.12). Because of the greater number of sampling intervals, the MLS wells showed more detailed trends of methane concentrations than the other devices. For iron, the MLS and piezometers often had comparable results; however, the tube samplers tended to show the highest concentrations (Figure 3.13). Sulfide was difficult to compare at these sites because there were fewer analyses and detections of sulfide. The shallower tube samplers and piezometers sometimes did not produce enough porewater to analyze for sulfide, and some of the MLS samples could not be analyzed because turbid samples interfered with the colorimetric sulfide analysis. The turbidity in MLSs possibly was from sealant contamination.

Figures 3.14, 3.15, and 3.16 show the concentrations of parent, daughter, and total VOCs at all six sites in June 2000, including sites WB34 and WB36 that show device comparisons at and below depths that the peepers could reach. General trends of decreasing parent VOC concentrations upward through the wetland sediment can be seen with each of the sampling devices at most of the sites (Figure 3.14). Exceptions include the increased or constant VOC concentrations in the tube samples from the shallow wetland sediment at site WB36 and in the MLS samples at site WB26 (Figures 3.14b, e). As discussed in the previous section, the high parent VOC concentrations in the tube samples at site WB36 could be from transport along macropores or other preferential flowpaths where biodegradation is limited. Site WB36 is in an area of focused ground-water discharge (Lorah et al., 1997; Lorah and Olsen, 1999b), which could account for the fact that this preferential flow effect is most apparent at this site (Figure 3.14). The MLS well at site WB26 most likely results from cross-contamination between sampling chambers. This was the only site where problems were encountered during installation of the MLS in the borehole, requiring removal and then reinsertion of the outer casing, reconstruction of the MLS, and reinsertion of the MLS in the casing. It is possible that cross-contamination resulted because the wetland sediments did not fully collapse on removal of the outer casing after its reinstallation and subsequent removal or that the bentonite packs did not expand sufficiently in the borehole.

As parent VOC concentrations decrease through natural attenuation (Figure 3.14), daughter product concentrations increase (Figure 3.15). Compilation of data from all the sampling devices indicates that greatest accumulation of daughter products occurs at depths of 50 and 200 cm below the wetland surface at the 6 sites (Figure 3.15). At most sites, this depth range corresponds to the upper peat unit of the wetland sediments (Figure 3.15). At site WB36, the extent of degradation would not have been obvious without the peeper samples (Figure 3.14b, 3.15b). Besides the peepers, the MLSs often showed trends in total VOCs and in production of metabolites in the most detail over this depth range because samples could be obtained more consistently from all the MLS sampling points than the tube samplers, and more screened

intervals were available than for the piezometers. The same trends in parent and daughter VOC concentrations with depth were observed in the March 2000 sampling as the June 2000 sampling.

### 3.3.3 Spatial Heterogeneity Experiment

The different sampling devices were installed within an approximately 1-m radius at each site. This lateral separation between the devices requires that spatial heterogeneities naturally present in the wetland sediments be considered when making comparisons among the sampling devices. To examine these potential heterogeneities, 3 peepers were inserted adjacent to each of the other three sampling devices at site WB36 so that comparisons could be made for spatial differences at a particular sampling location (Figure 3.16 to 3.18). The peepers were spaced 0.9 m laterally apart from each other in a line extending perpendicular to the creek from site WB36, with the peeper by the piezometer nest located the greatest distance from the creek and the peeper by the tube sampler nest closest to the creek (Figure 3.1). Concentrations of the parent VOCs (TCE and PCA) were less than  $0.04 \mu\text{mol/L}$  at all three locations of the peepers, and the daughter compound VC comprised most of the total VOC concentrations (Figure 3.16 and 3.17). Thus, the total VOC trends were similar to those of VC. Overall, the peeper at the piezometer location had the lowest concentrations of VOCs, whereas the peeper at the MLS location had the highest concentrations (Figures 3.16 and 3.17). The distributions of the parent and daughter VOCs were approximately the same in the peepers installed at the MLS and tube samplers at site WB36 for the spatial heterogeneity experiment (Figure 3.17). Based on these results, natural spatial variability does not explain the exceptionally high PCA and TCE concentrations that were measured in the tube samplers compared to the other devices in March and June 2000 (Figures 3.10a and 3.11a). VOC concentrations among the 3 peeper locations showed the greatest variability at depths of 0 to 35 cm below land surface (Figure 3.16). Total VOC concentrations differed by a maximum of about  $0.6 \mu\text{mol/L}$  in the 0 to 35 cm depth range, whereas they differed by a maximum of about  $0.2 \mu\text{mol/L}$  in the 35 to 60 cm range. Because few screened intervals were placed in the upper 35 cm for the other sampling devices (Table 3.1), local spatial heterogeneities likely had minimal effect on the comparisons discussed for the different sampling devices in the preceding sections. When comparing concentrations of VOCs and redox constituents among the different sampling devices, an overall trend of decreasing variability with depth was observed also.

There are numerous factors that could cause a higher variability of VOC concentrations in the upper 35 cm of the wetland sediment, including increased density of plant roots that could affect natural organic substrates, local redox conditions, microbial community structures, and preferential flowpaths. In addition, tidal effects on local contaminant transport also may be greatest in this shallow region of the wetland sediments. The lower concentrations of VOCs at the peeper placed by the piezometers compared to the other two locations (Figure 3.17) could result from less upward discharge of VOCs from the aquifer by the piezometers or from increased biodegradation rates in the wetland sediments at this location. Because site WB36 is near the creek channel where reversals in ground-water-flow directions have been observed in the wetland sediments in a previous study (Lorah et al., 1997), differences in upward discharge may be the dominant factor in the lower VOC concentrations at this piezometer location.

For the redox-sensitive species, methane and ferrous iron concentrations showed the least variability among the peepers installed at the 3 locations (Figure 3.18). The consistent methane concentrations indicate that local spatial heterogeneities were not a dominant factor in the lower

methane concentrations that were often observed in the piezometers and tube samplers compared to the peepers and MLSs in the shallow wetland porewater (Figures 3.7, 3.8, and 3.9). Sulfide was the most variable redox constituent in the spatial heterogeneity experiment (Figure 3.18).

Overall, greater spatial variability was observed among the 3 peeper for the VOCs than for the redox-sensitive species. Production of the redox-sensitive species in the naturally organic-rich wetland sediments is independent of the influx of contaminants from the aquifer. In contrast, the distribution of VOCs in the wetlands is controlled partly by the rate and path of ground-water flow from the aquifer and through the wetland sediments. The greater local heterogeneity in VOCs, therefore, may be attributed to the plume configuration in the aquifer, the location of macropores such as root channels that would act as preferential flow paths through the wetland sediment, and small-scale variations in ground-water-flow directions and rates from tidal influences. When sampling in a wetland environment, it is not only important to obtain a fine vertical resolution, but closely spaced samples should also be obtained laterally.

### **3.3.4 Water-level Measurements**

Synoptic water-level measurements were conducted at the MLS wells and piezometers on March 7 and June 12, 2000 at all six sites (WB23, WB24, WB26, WB30, WB34, and WB36). The water levels were generally lower in the MLSs compared to the piezometers (Figure 3.19). On both dates, about 70 percent of the MLSs had lower water levels than the piezometers screened at comparable depths. On March 7, the mean water levels for the piezometers and MLSs, respectively, were 0.56 and 0.82 m below land surface; on June 12, mean water levels for the piezometers and MLSs, respectively, were 0.57 and 0.65 m below land surface. The small diameter of the sample chambers in the MLSs apparently causes inaccurate water-level measurements.

### **3.3.5 Technical and Logistical Considerations**

In addition to assessing the quality of chemical data obtained from this device comparison study, technical, logistical and cost comparisons also need to be addressed for a thorough evaluation of a method selection process (Table 3.2). When performing field evaluations in a wetland setting, logistics and costs of heavy equipment necessary for drilling and well installation must be considered. Wetlands are ecologically sensitive areas and special precautions are needed to avoid causing detrimental effects to the environment or its wildlife. Planning the movement and placement of drilling equipment at the APG sites posed the greatest obstacle to well installation. Portable drill rigs or devices needing only manual power were used in this study to limit these problems. For installation of the MLS wells, a portable vibracore drill rig that could be carted on a small hand truck was used, allowing it to be maneuvered across the floating walkways that line the transects through the study area (Figure 3.3b). Because power decreases with the size of the drill rig, sediment core collection and MLS installation could be performed only at relatively shallow depths (less than about 8 m). A sturdy support platform that could be easily moved to the different sites was constructed to support the drill rig during drilling operations. Because sand packs and bentonite seals between ports were affixed to the well unit itself, no borehole filling or grouting was necessary for the MLSs. A week was required to assemble and install six MLSs. No drilling was necessary for installation of the drive-point piezometers. The piezometers were manually driven using a slide bar hammer or a gas-powered

vibrating hammer operated by two people. These relatively narrow-diameter wells did not significantly disturb the marsh sediment or aquifer material during their installation, and therefore did not require bentonite fill or cement grout sealing, nor did they require any well development to stabilize the material surrounding the wells.

**Table 3.2. Comparison of Sampling Devices**

Sampling Device	Advantages	Disadvantages
Drive-Point Piezometer	<ul style="list-style-type: none"> <li>• Shallow/moderate depth multi-level sampling</li> <li>• Fe results generally similar to peepers</li> <li>• Generally good comparisons to other devices at &gt;100 cm depths</li> <li>• Able to obtain hydraulic parameters</li> <li>• Moderate expense/maintenance</li> <li>• Moderate ease of installation</li> </ul>	<ul style="list-style-type: none"> <li>• VOC concentrations generally lower than peepers</li> <li>• VOCs and redox species subject to aeration at shallow depths</li> <li>• May draw water from other areas during sampling</li> <li>• Can create channeling if well diameter too large or too close</li> <li>• May reflect local spatial heterogeneities because of nest</li> <li>• Slow recovery after purging in wetland sediments</li> </ul>
Tube Sampler	<ul style="list-style-type: none"> <li>• Shallow depth multi-level sampling</li> <li>• Total VOC results similar to peepers</li> <li>• Fe good at depth compared to other devices</li> <li>• Assesses potential impact from macropore flow</li> <li>• Low expense/maintenance</li> <li>• Ease of installation (no drilling)</li> </ul>	<ul style="list-style-type: none"> <li>• Interception of macropore flow may obscure biodegradation reactions occurring in rest of wetland sediments</li> <li>• Difficult to sample because of low well volume</li> <li>• Unable to obtain hydraulic parameters</li> <li>• May reflect local spatial heterogeneities because of nest</li> <li>• Can easily move up or down unless well-anchored at land surface</li> <li>• Slow recovery after purging</li> </ul>
Peeper	<ul style="list-style-type: none"> <li>• Shallow depth multi-level sampling</li> <li>• Gives the best vertical resolution of porewater chemistry</li> <li>• Best indicator of porewater chemistry (highest overall VOC and redox-sensitive concentrations)</li> <li>• Least affected by spatial heterogeneities because of diffusion</li> <li>• Less chance of aeration during sample removal and no recovery time problems</li> <li>• Large number of porewater samples collected simultaneously</li> <li>• Ease of use (no drilling) and inexpensive to install</li> <li>• Mobile, reuseable</li> </ul>	<ul style="list-style-type: none"> <li>• Small sample volume; unable to repeat sampling without reinstalling</li> <li>• Labor intensive/time consuming for preparation</li> <li>• Unable to obtain hydraulic parameters</li> <li>• Difficult to insert/remove in semi-dry or tight sediments, or where tough roots are present</li> <li>• Porous membrane expensive but overall are least expensive in terms of material and installation</li> <li>• Repeated installation and removal at same site disturbs sediment</li> </ul>
Multi-Level Sampler	<ul style="list-style-type: none"> <li>• Shallow/moderate depth multi-level sampling</li> <li>• Methane results similar to, or greater than, peepers</li> <li>• Discrete vertical increments without effects from lateral spatial heterogeneities as may be observed in clustered samplers</li> <li>• Able to obtain hydraulic parameters</li> <li>• Fast recovery after purging</li> <li>• Ease of sampling—7 depths in one borehole</li> </ul>	<ul style="list-style-type: none"> <li>• VOC results lower than other devices at shallower depths</li> <li>• Bentonite and chamber sealants may affect results</li> <li>• Possible problems with inadequate seals between bentonite packs</li> <li>• Possible cross-contamination by diffusion through polyethylene</li> <li>• Drilling equipment required (difficult logistics in wetlands)</li> <li>• High initial cost</li> </ul>

The tube samplers and peepers were installed manually by one person, but these devices can be used only for shallow sampling in relatively soft sediment. No drilling or mechanical devices are required for installation of these devices. Occasionally, peepers are difficult to remove in tight sediments. In these instances, the peepers were withdrawn from the sediments using a simply constructed wooden and rope lever (Figure 3.5a). Although initially somewhat expensive to construct, the peepers are mobile sampling devices (allowing placement where and when desired) and can be reused innumerable times with only the additional cost of the porous membrane paper that covers both sides of the peeper. The peeper's mobility is a distinct advantage compared to the other devices; however, repeated installation and removal at a particular site may disturb the sediments. The tube samplers were the least expensive and complicated of the devices to construct and install.

Obtaining sufficient sample volumes for the analysis of all desired chemical parameters was a drawback with most of the devices. However, considering the physical characteristics of most wetland sediments, the use of almost any device would pose these same problems. A minimum volume of 40 ml, plus 5-10 ml for vial wash where necessary and initial waste of first-drawn water (to eliminate possible aerated water from the initially drawn water through the sampling tube), were required for the collection of duplicate VOC, methane, iron, and sulfide samples for each well. This minimum volume assumes a relatively high concentration of iron and sulfide in the porewater sample so that dilutions may be performed for these species. An additional 36 ml of sample were required for undiluted iron and sulfide analysis in cases where sample concentrations were low.

Of the four devices, the tube samplers delivered the lowest porewater volumes. Given their small well diameters, it was often difficult to extract the necessary volumes for analysis of all constituents, particularly in the shallower wells. Because of the fine sediments through which samples were drawn, some tube samplers did not recharge after purging in a timely manner to obtain all of the desired samples. In most instances, these wells yielded only enough ground water to sample for VOCs, methane, and iron. The chambers of the short peepers contained just enough sample volume to analyze the VOCs and major redox constituents. If a membrane rupture occurred in a particular chamber, only one VOC sample was obtained. The long peeper contained larger chambers and therefore, sufficient volumes were available to perform the critical analyses and also to collect for additional constituents such as dissolved organic carbon, chloride, and sulfate. The piezometers usually held enough water to obtain samples for all constituent analysis; however, as in many of the tube samplers, recovery after purging was very slow in some of the shallow piezometers. The MLS wells were the most productive of the four devices. The channels were of adequate diameter to hold sufficient ground water for sampling, and because sand packs surround each of the sampling ports, relatively fast recovery occurred during purging.

Lateral spatial heterogeneities in the wetland sediments would not complicate chemical or physical evaluations of the MLS samples at a site because a single borehole is used to accommodate up to seven sampling ports at various depths. In contrast, the piezometers and tube samples were installed in clusters that could show effects of local spatial heterogeneities, especially at depths less than 35 cm (Figure 3.16). However, based primarily on VOC results, four potential problems with the material and construction of the MLS wells became apparent: (1) chemical compounds from the bentonite and chamber sealants likely were the cause of some interference problems with the GC/MS analysis of VOCs and the colorimetric analysis of sulfide, (2) cross-contamination and/or leakage between chambers at site WB26 likely resulted from



inadequate seals between the bentonite packs, and (3) spill-over of water between chambers is possible when hydraulic heads are high (channel extensions were added to some well chambers to prevent this problem). Cross-contamination also could occur by diffusion through the polyethylene chamber walls; however, sufficient purging immediately prior to sampling eliminated this potential effect.

Because of the closely spaced intervals of the peeper chambers, a fine vertical resolution is obtained in the shallow wetland sediments where the majority of the biodegradation reactions are occurring. Compared to other devices, there is less chance for sample aeration with the peepers because: (1) samples are passively collected into chambers filled with water and no recovery time is needed, (2) tubing does not have to be inserted through a narrow diameter water column, and (3) water samples do not have to be pulled from depth as in the other sampling devices. The numerous chambers allow for a large number of porewater samples to be collected simultaneously so that temporal variations are not incurred.

The drive-point piezometers are the only device that was tested that could be used for accurate water-level-measurements. Although water levels were measured in the MLSs, values did not compare well with the larger diameter drive-point piezometers (Figure 3.19). In addition, the small chamber diameters of the MLSs could not accommodate pressure transducers for continuous water-level monitoring.

### 3.4 Evaluation of a Voltammetric Microelectrode

Electrochemical measurements of iron and sulfide at site WB35 compared relatively well with standard chemical analyses of these constituents in peeper samples (Figure 3.20). Oxygen measurements also were made, but it was detected only in the upper 3 cm. *In situ* microelectrode measurements made in the sediment adjacent to a peeper before its removal from the sediment compared showed the same general trends in iron and sulfide concentrations with depth as microelectrode measurements made in the peeper cells after its removal from the sediment. Peeper sampling was done in a glove bag filled with a nitrogen atmosphere to limit oxidation of reduced iron and sulfide during measurement. However, concentrations of these redox constituents in the upper 30 to 40 cm were higher in the *in situ* microelectrode measurements than in the peeper cell measurements, indicating some loss of constituents during peeper sampling (Figure 3.20). Below about 40 cm, *in situ* microelectrode measurements showed iron and sulfide concentrations decreasing to below detection levels, whereas the measurements in the peeper cells (both with the microelectrode and by standard chemical analyses) showed detectable iron and sulfide. The reason for this discrepancy at greater depths is unclear. Damage to the microelectrodes from pushing into the sediment was discounted because calibration curves made with the microelectrodes after their removal from the sediment agreed with calibration curves made prior to the field test. *In situ* microelectrode measurements made at site WB19 on two different dates showed detectable iron and sulfide concentrations to depths of about 52 cm (Figure 3.22). Manganese concentrations determined in peeper cells using the microelectrode were about the same as those measured using standard chemical analyses of the porewater at depths of about 30 to 55 cm (Figure 3.22). Manganese was not detected with the microelectrode in the upper 28 cm of peeper cells, possibly because interference from another compound at these depths obscured the manganese peaks.

These data indicate great potential for the electrochemical/microelectrode system to characterize redox conditions in shallow sediments, although additional study is needed to

investigate some discrepancies that were observed between the microelectrode measurements and standard chemical measurements. No other reports of *in situ* voltammetric microelectrode measurements made at depths greater than about 10 cm could be found in the literature. The tests presented here indicate that *in situ* measurements to at least 50 cm is feasible in wetland sediments with the epoxy-filled glass microelectrodes. Microelectrode measurements could be valuable because much of the biodegradation occurred within the upper 50 cm of the wetland sediment and withdrawal of porewater samples with devices other than peepers was difficult at these shallow depths. The primary advantages of the microelectrode system are: (1) analyses are rapid (approximately 3 minutes was required at each depth or peeper cell to scan for oxygen, iron, manganese, and sulfide); (2) the sample is the least disturbed from its natural setting (particularly in the *in situ* mode of operation), which is important for limiting oxidation or volatilization of redox-sensitive species; and (3) multiple constituents can be measured at extremely small-scale depth intervals without removing porewater or sediment for analyses. Currently, the primary disadvantage is that the microelectrode system for environmental work still is in a research phase and requires a fairly intensive time commitment to learn how to construct and calibrate microelectrodes, operate the electrochemical analyzer, and interpret the voltammetric measurements.

### 3.5 Summary and Conclusions

A variety of sampling devices should be included in any wetland study to ensure reliable contaminant and redox data. Depending on the specific chemical and hydraulic parameters required at a site, some devices might be preferable to others. In a comparison of four sampling devices used at a wetland contaminated by chlorinated solvents, peepers were the most reliable and gave the best overall indication of redox conditions and VOC concentrations in the shallow wetland porewater, where much of the biodegradation reactions were occurring. If the wetland sediments are thicker than 120 cm (the longest peeper that was tested), other sampling devices will also be necessary. At depths greater than about 100 cm, concentrations of VOCs and redox constituents measured with the different sampling devices were more consistent than at shallower depths. Drive-point piezometers may be needed to reach deeper depths and to obtain water level measurements, but chemical data for volatile and redox-sensitive constituents obtained from piezometers in shallow anaerobic wetland sediments must be interpreted with caution. Preferential flow paths (such as those through root channels) could cause locally high concentrations of VOCs that have not undergone degradation. Tube samplers may be beneficial in assessing the impact from this preferential flow. Additional experimentation and sampling could result in a better understanding of transport mechanisms in wetland sediments and the flowpaths intercepted by different sampling devices.

Local spatial heterogeneities should be considered when assessing wetland contaminant data. Depending upon the physical nature of each wetland site, practical considerations such as technical, logistical, and cost evaluations also need to be included in determining the choice of sampling device. *In situ* measurements for redox constituents with a voltammetric microelectrode system compared well with standard chemical analyses and indicated that further development of this tool for redox characterization in wetlands or other shallow sediment environments is warranted.



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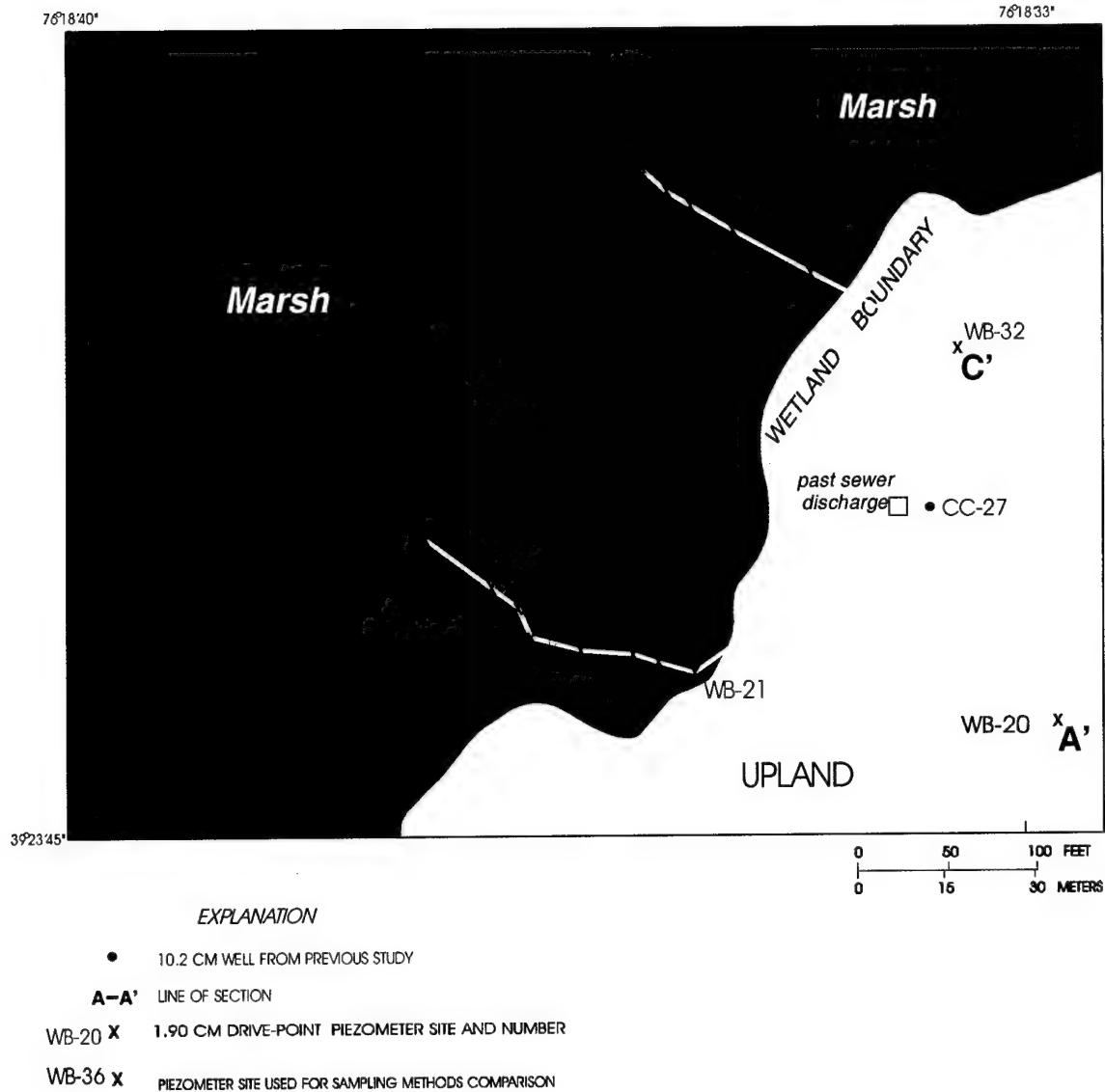


Figure 3.1. Locations of drive-point piezometer sites that were present at West Branch Canal Creek wetland site prior to the ESTCP study and of sites used for the comparison of sampling methods for the ESTCP study.

Sample Port  
Unit

Shield

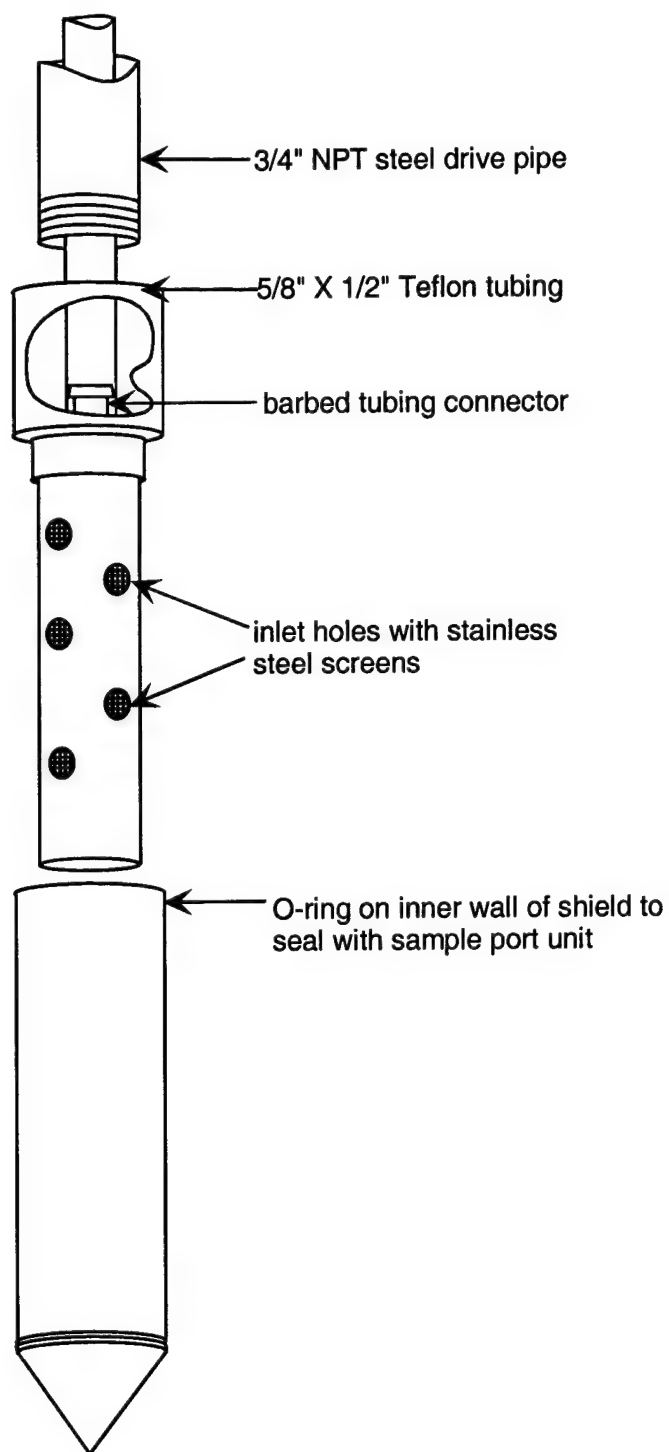
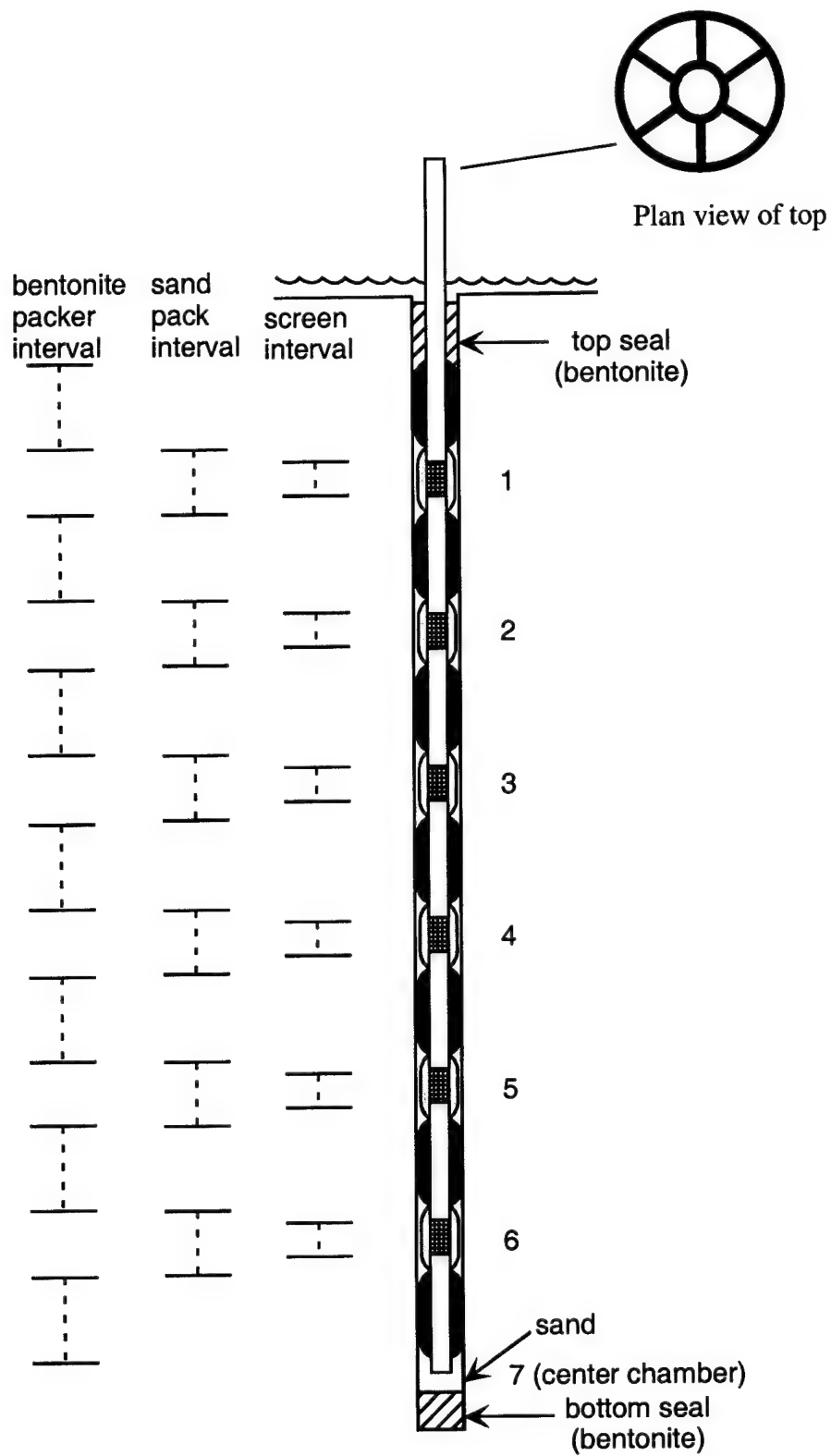


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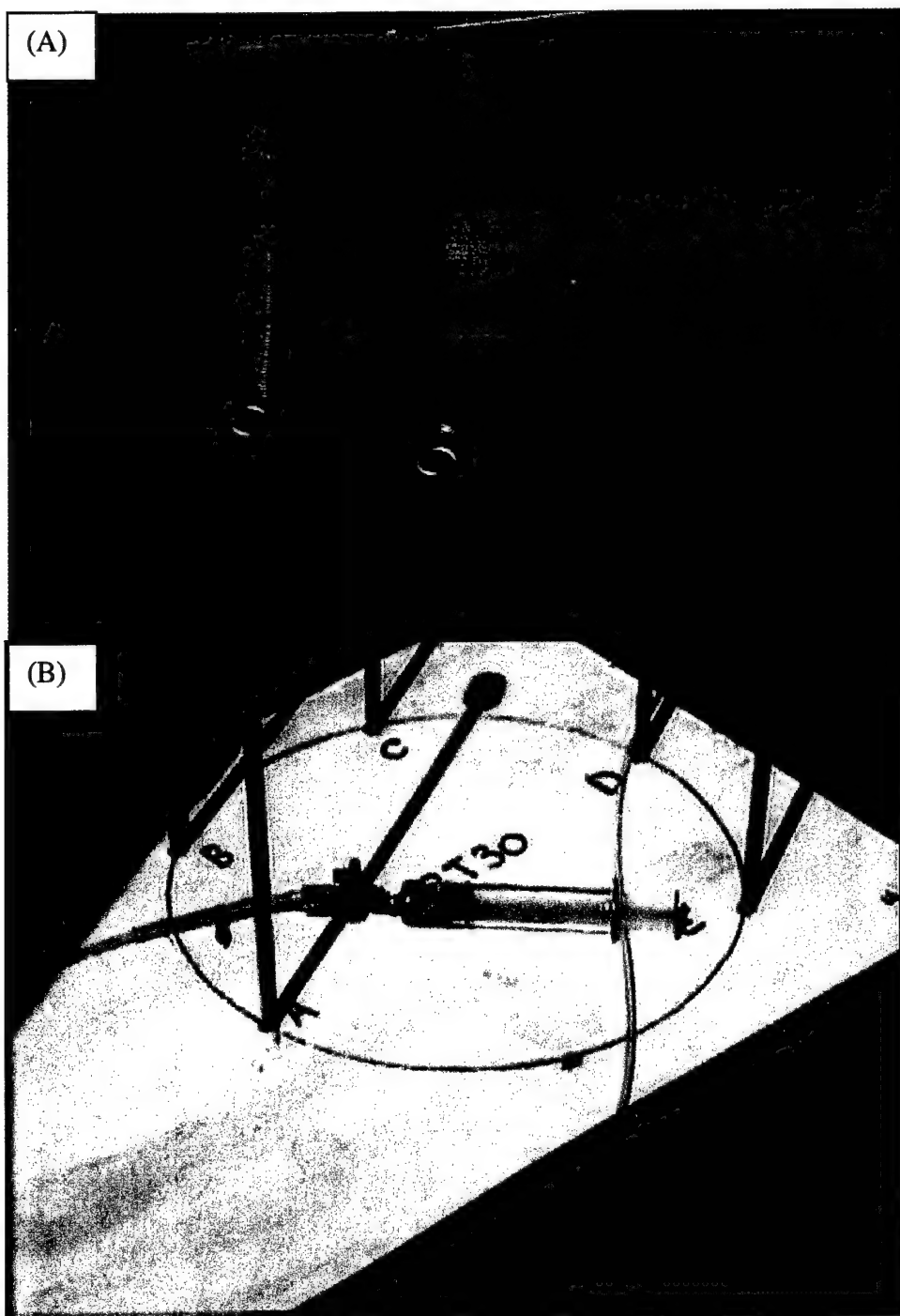


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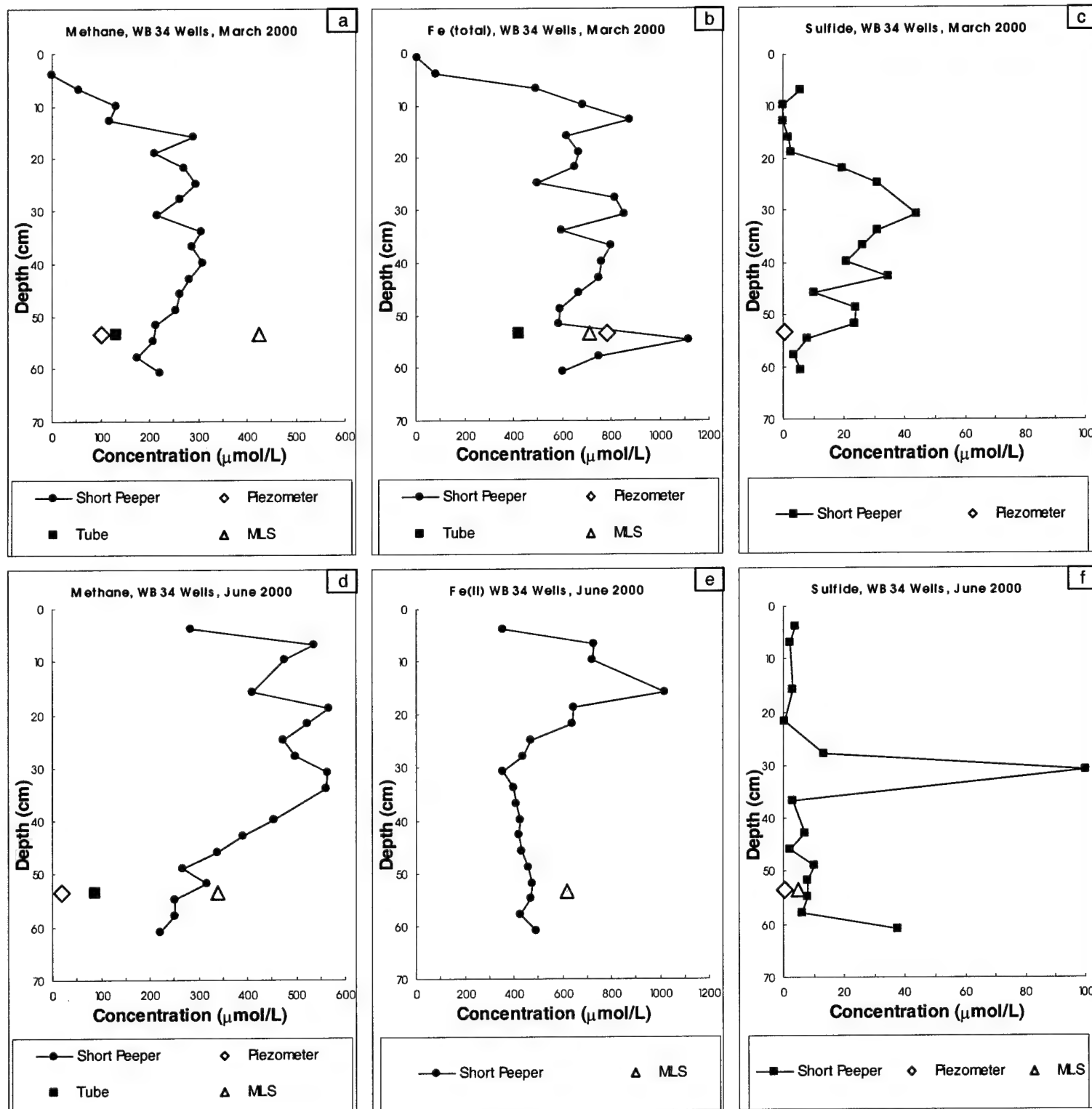


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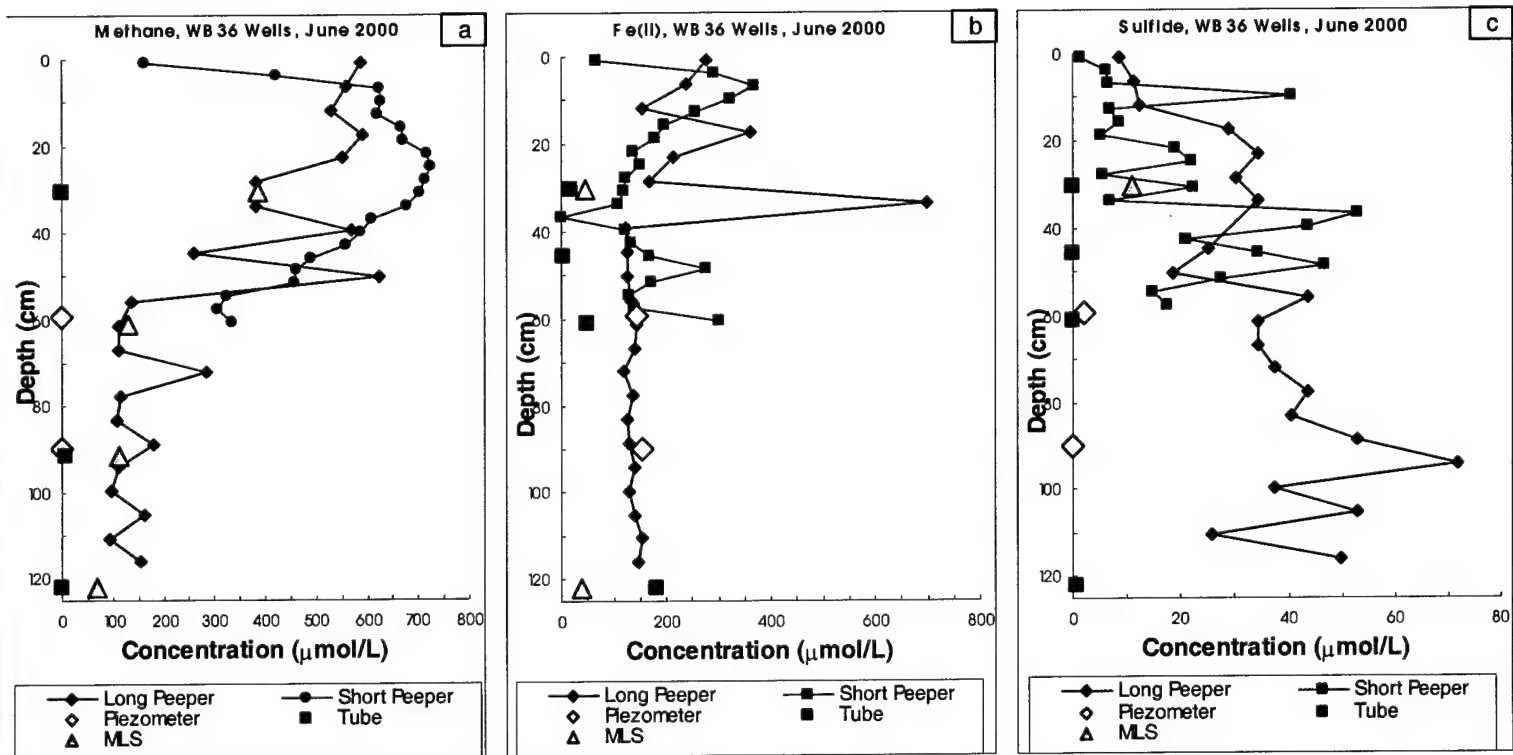


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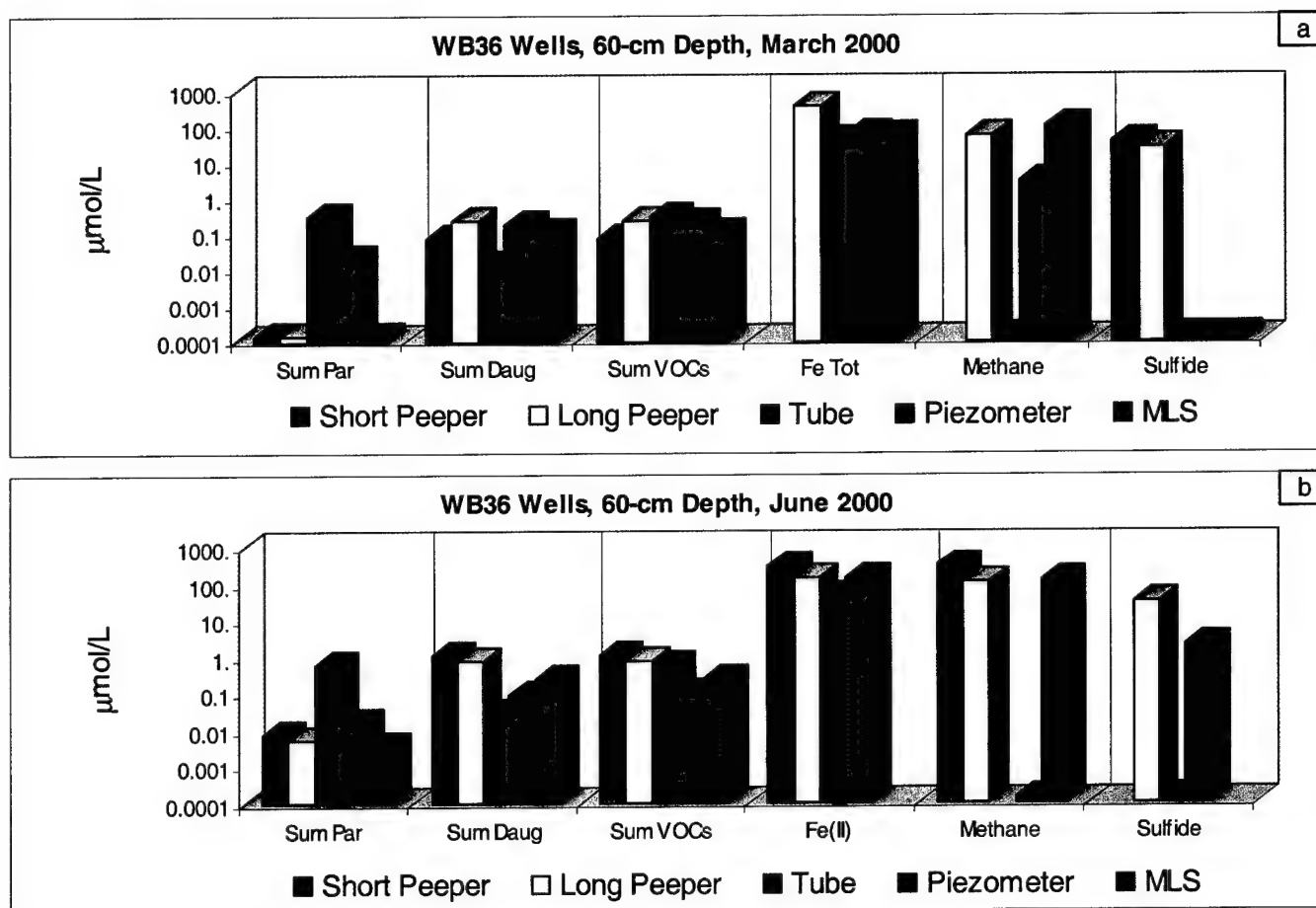


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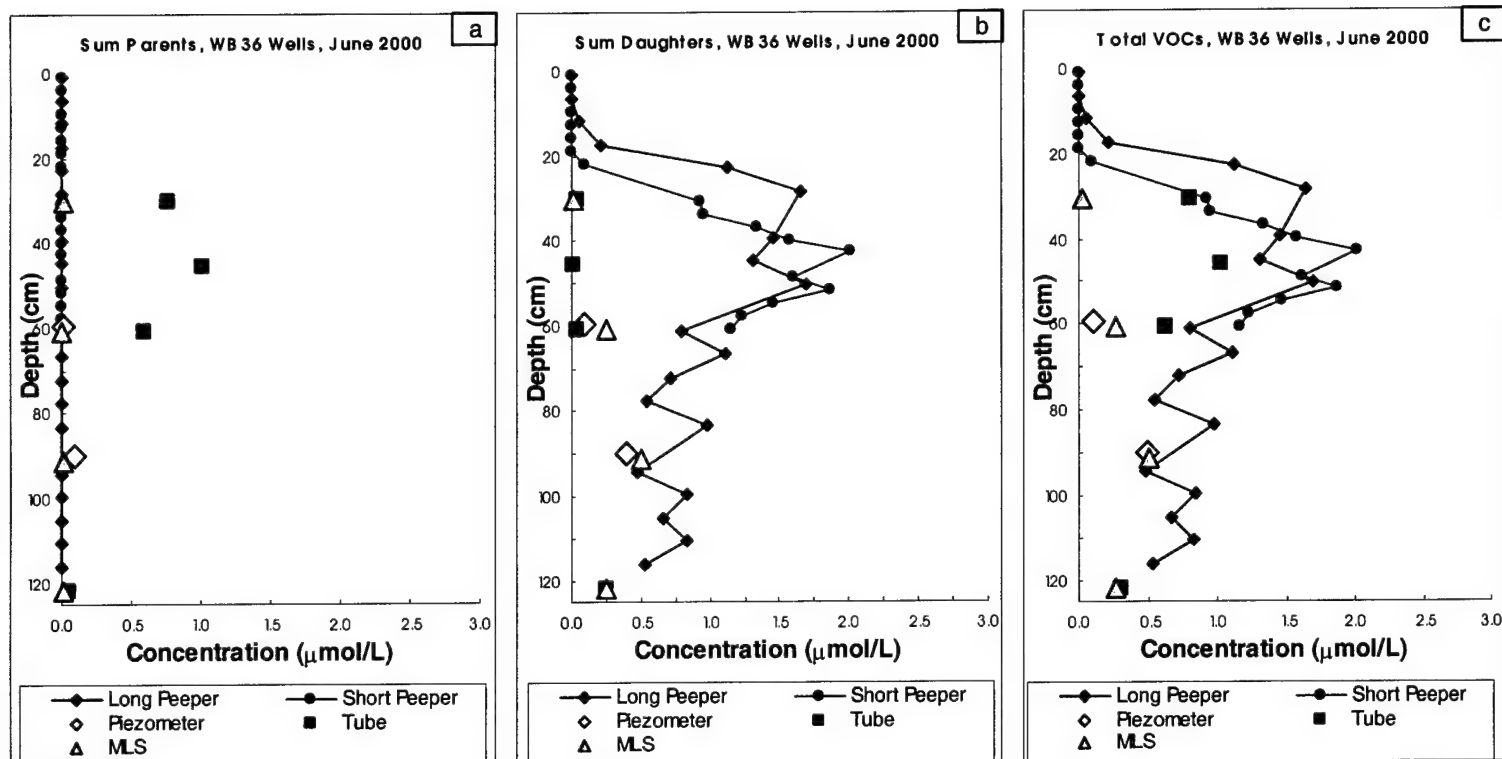


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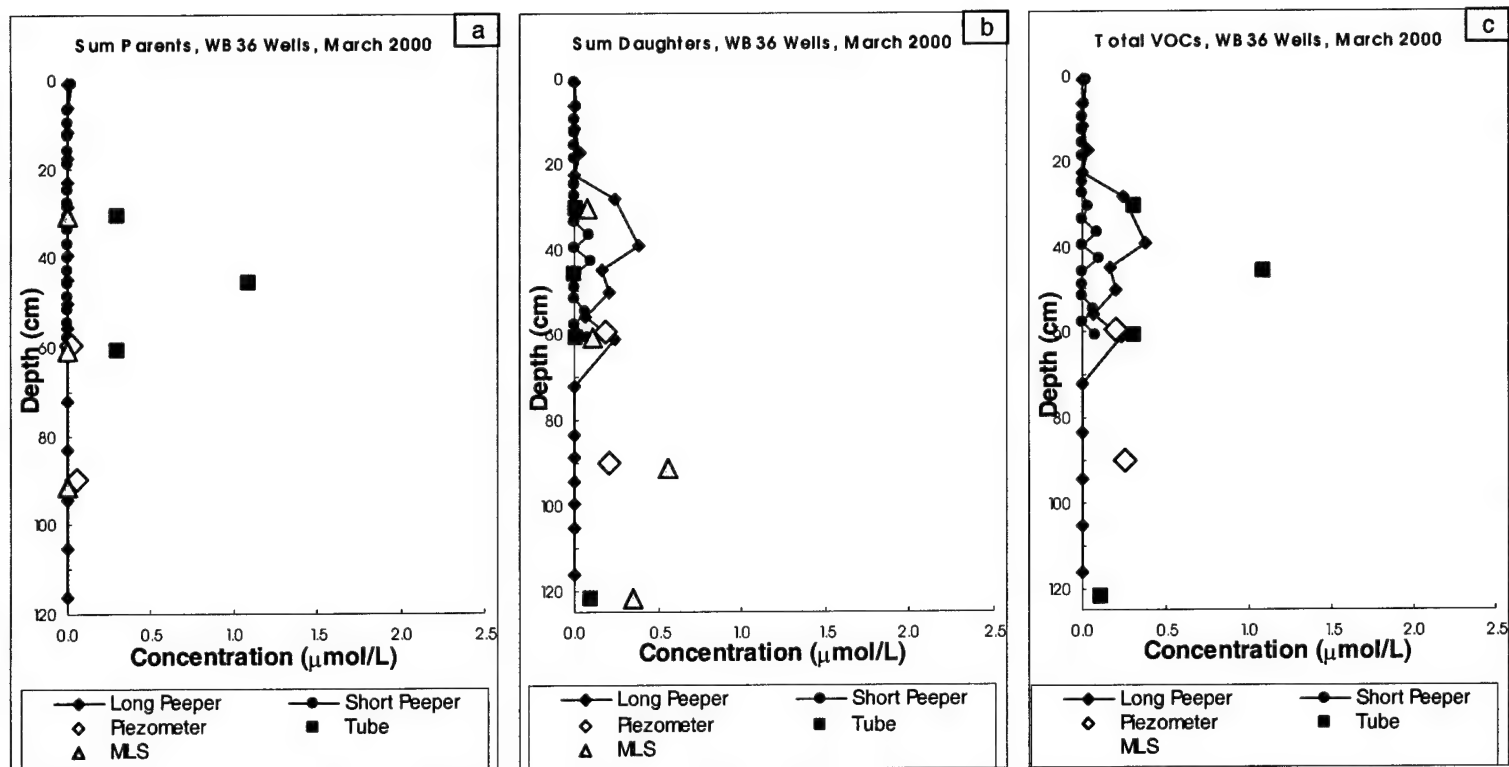


Figure 3.11. Concentrations of parent VOCs, daughter VOCs, and total VOCs in samples collected from peepers compared to other sampling devices installed at site WB36, March 2000.



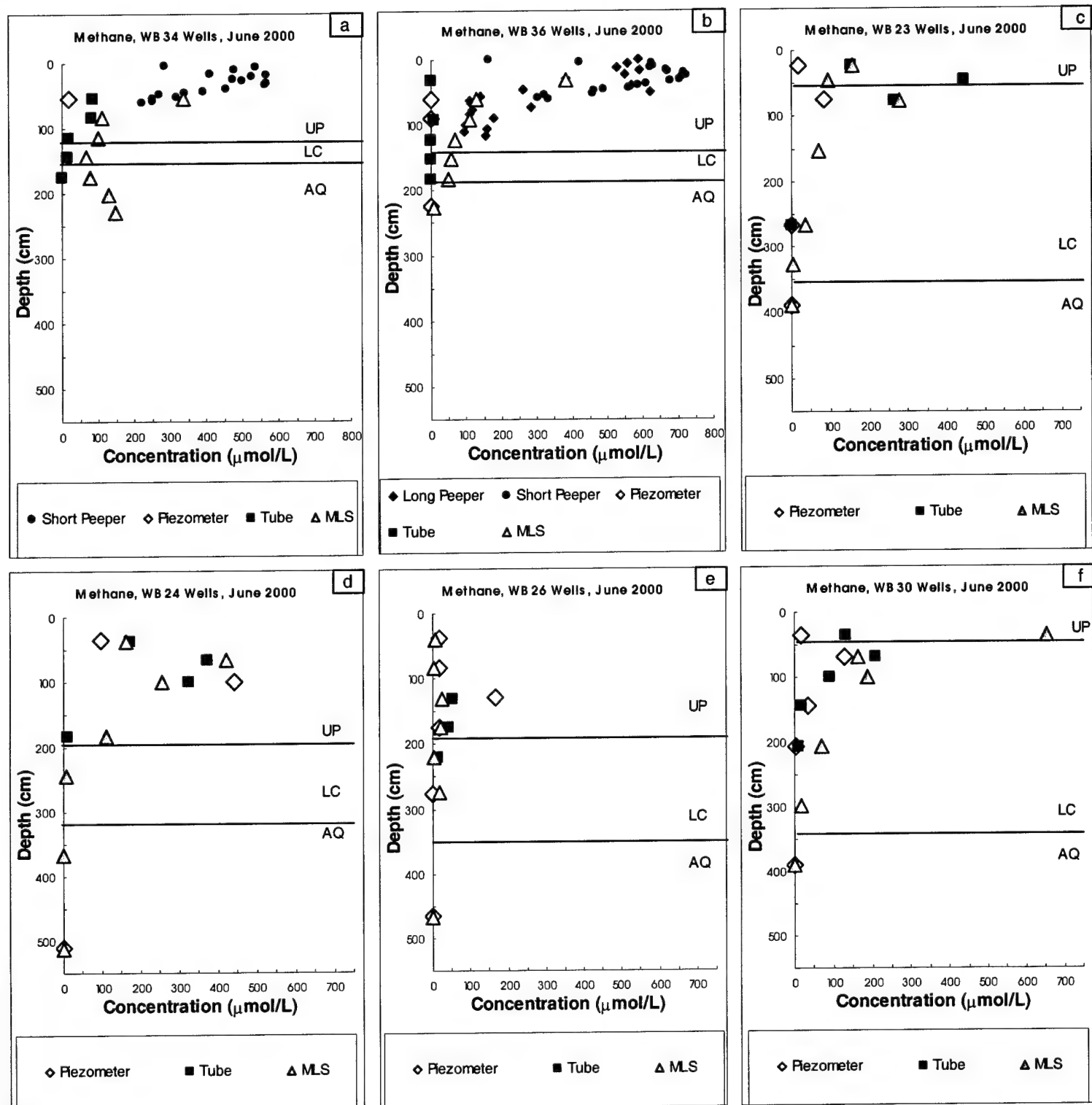


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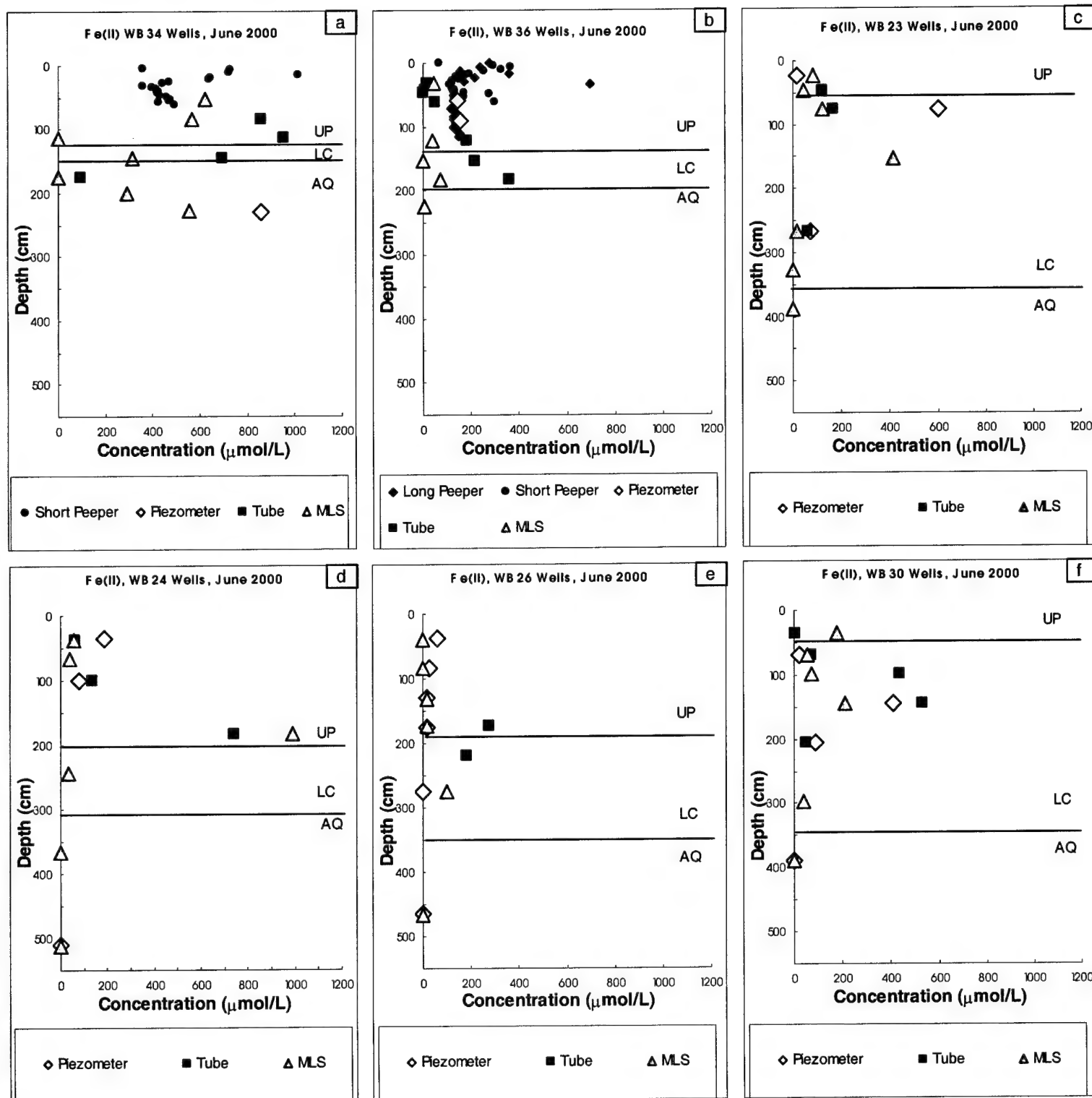


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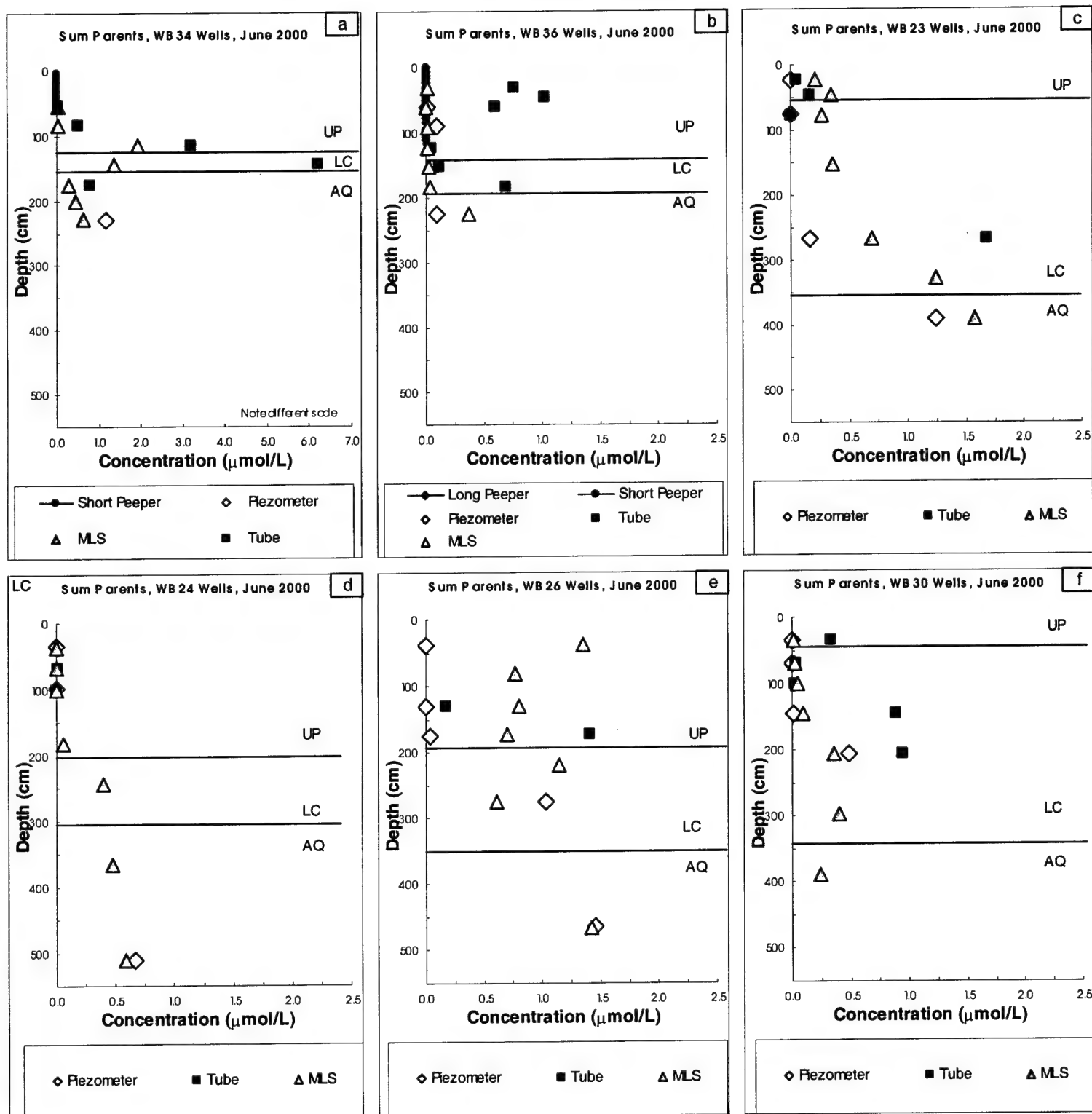


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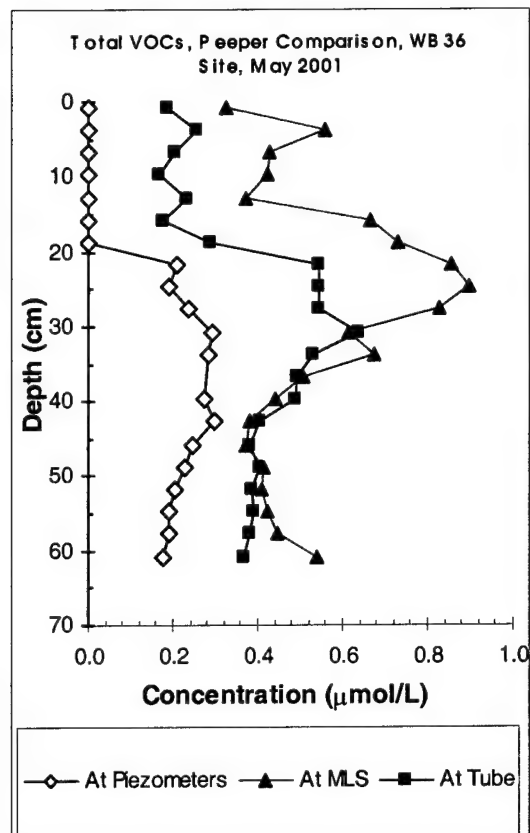


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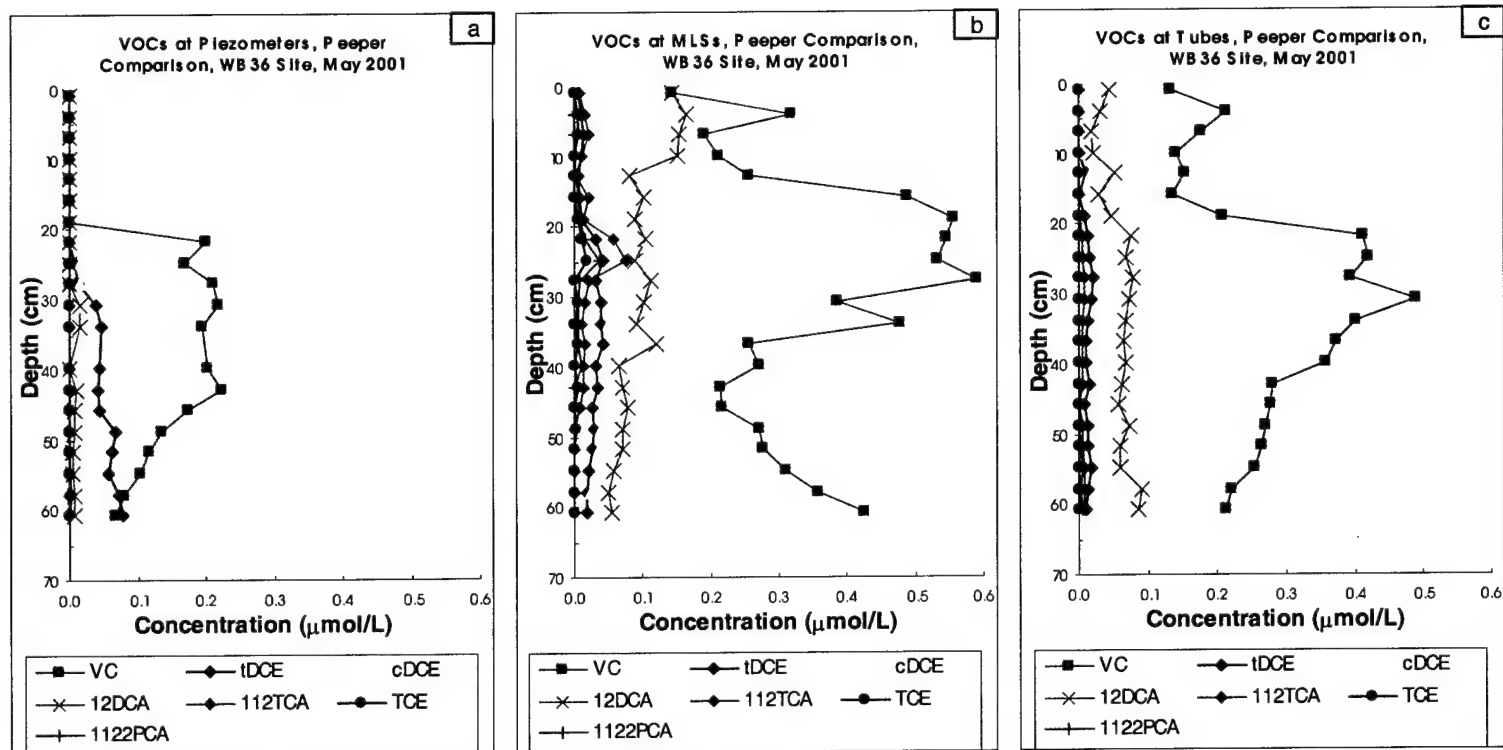


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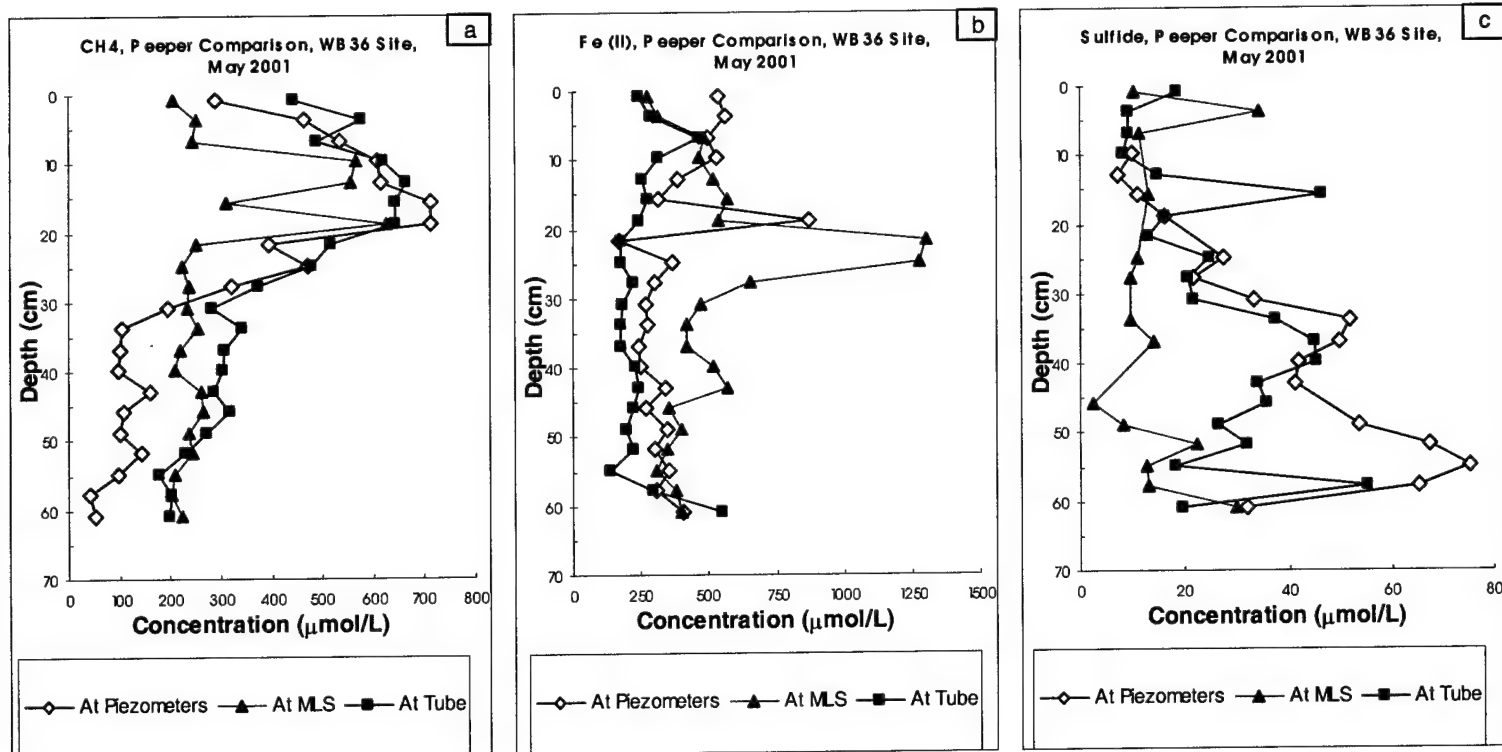


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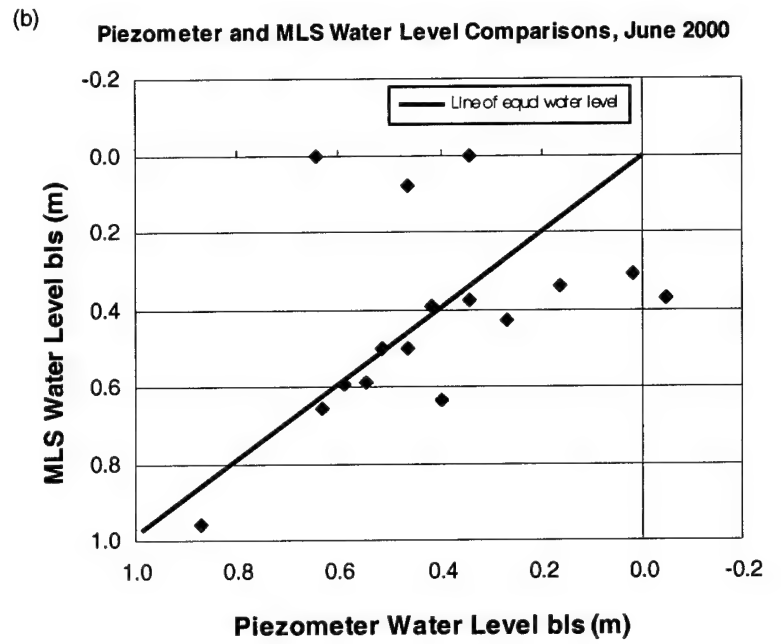
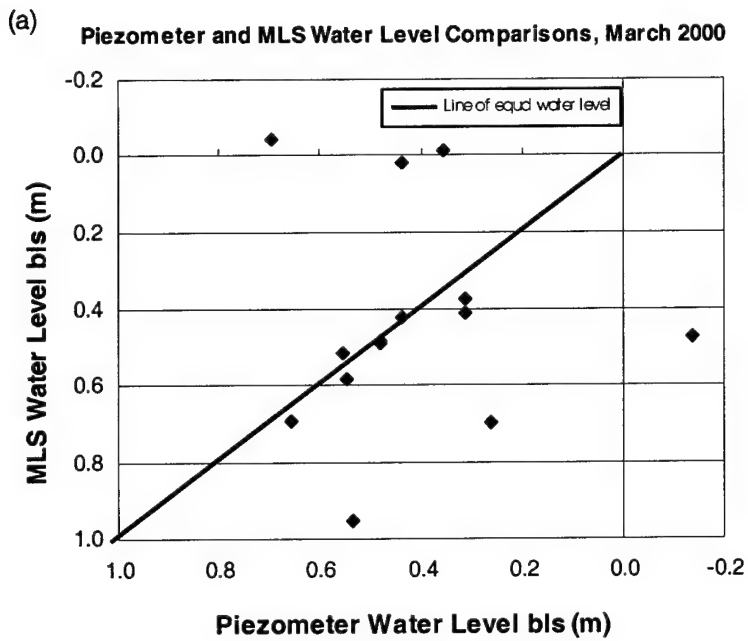
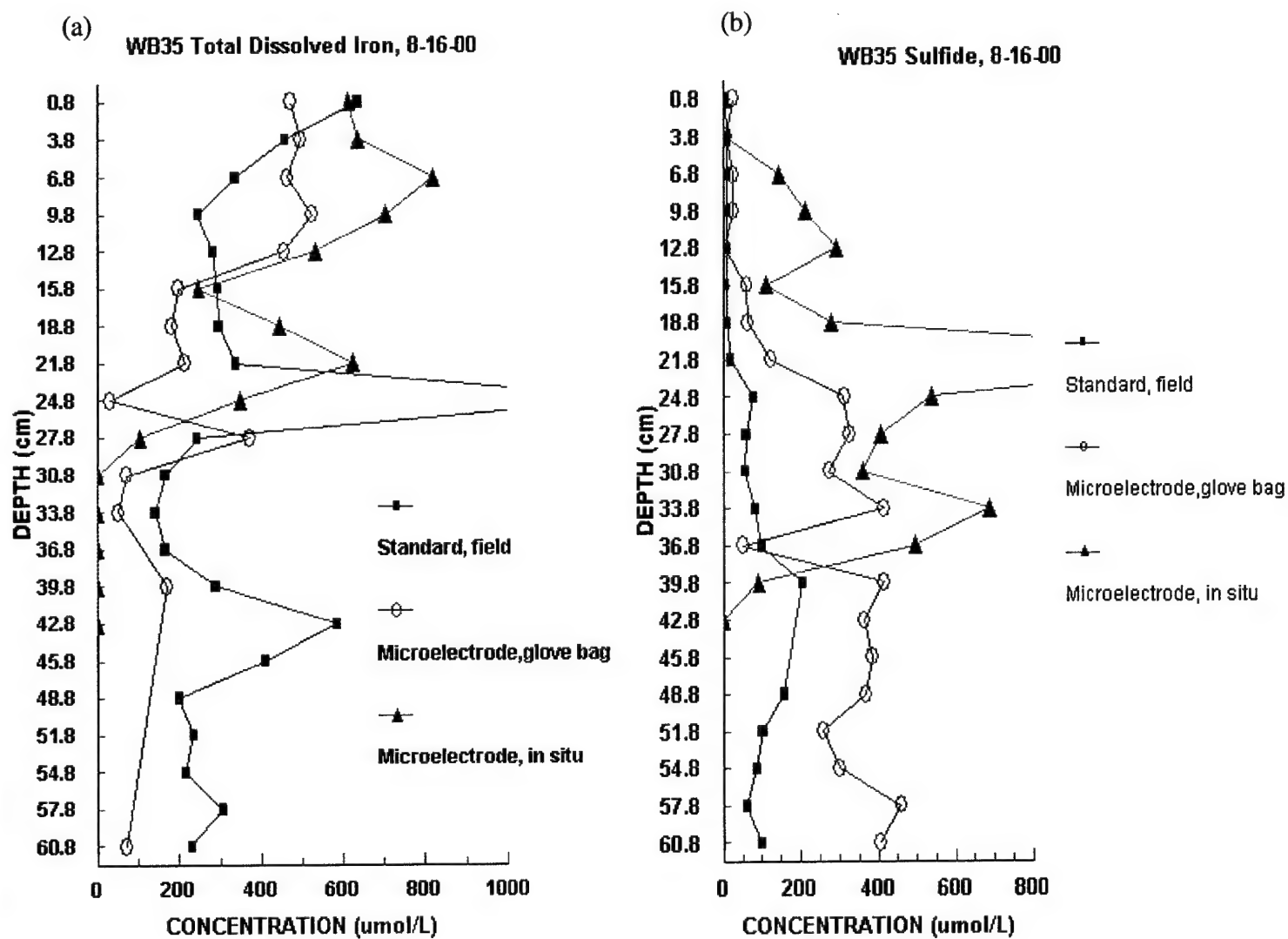
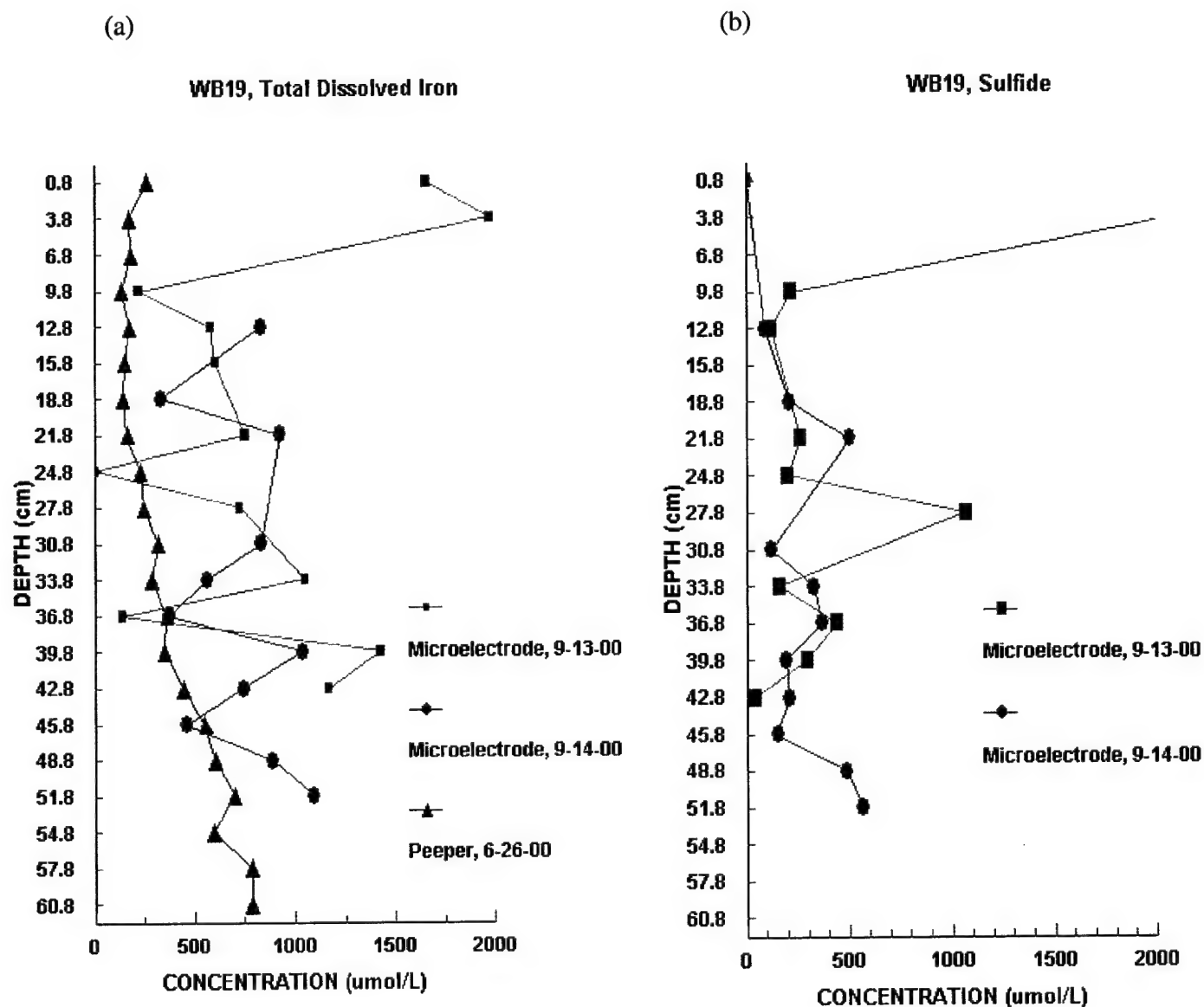


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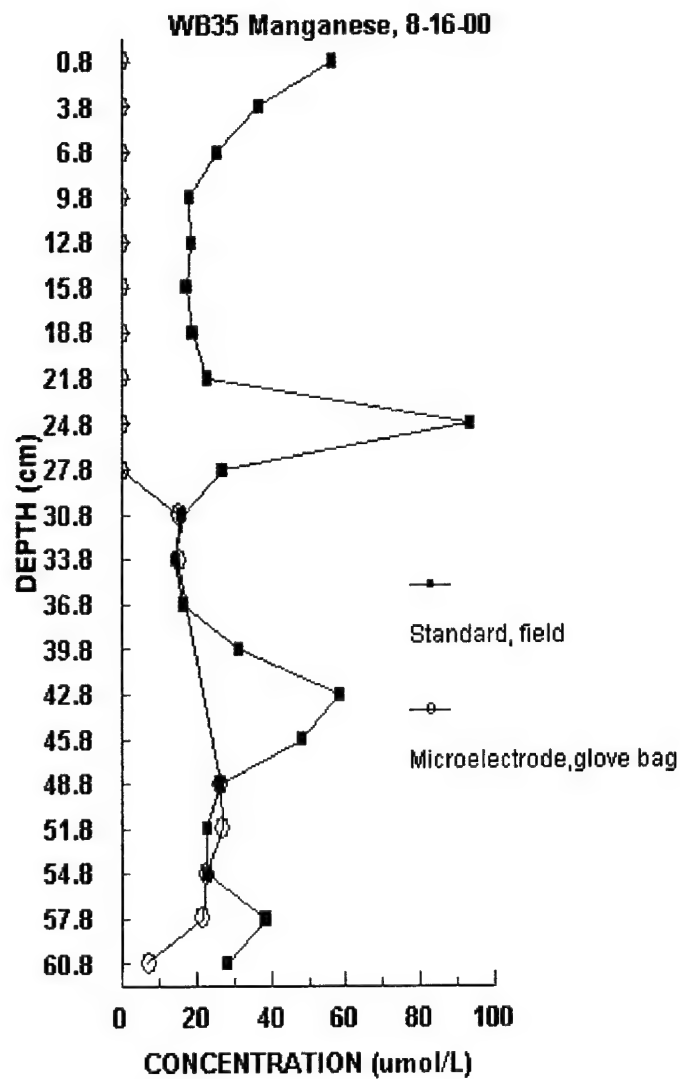




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## **Section 4. Draft Technical Protocol for Characterizing Natural Attenuation of Chlorinated**

### **Solvent Ground-Water Plumes Discharging into Wetlands (An Addendum to the AFCEE**

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## **Section 4. Draft Technical Protocol for Characterizing Natural Attenuation of Chlorinated Solvent Ground-Water Plumes Discharging into Wetlands**

### **(An Addendum to the AFCEE Chlorinated Solvent Natural Attenuation Protocol (Wiedemeirer et al., 1996))**

#### **4.1 Introduction and Background**

The U.S. Environmental Protection Agency has defined *natural attenuation* as: “naturally-occurring processes in soil and ground-water environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants.” Natural attenuation as a remedial action alternative for contaminants dissolved in ground water has gained considerable acceptance in recent years, particularly with respect of dissolved petroleum hydrocarbons (Stauffer et al., 1993; Weidemeier et al., 1994; National Research Council, 2000). In aquifers, trichloroethene (TCE) and other chlorinated solvents tend to be relatively resistant to transformations, either biotic or abiotic, compared to the biodegradation potential of petroleum hydrocarbons. Reductive dechlorination is the most important biodegradation process for the more heavily chlorinated ethenes such as TCE and tetrachloroethene (PCE). In reductive dechlorination, the chlorinated solvent acts as an electron acceptor and is sequentially reduced to lower chlorinated compounds. Reductive dechlorination of PCE and TCE occurs primarily by sequential hydrogenolysis to 1,2-dichloroethene (12DCE), vinyl chloride (VC), and ethene (Vogel and McCarty, 1985; Freedman and Gossett, 1989; Bouwer, 1994). Because this biodegradation process can result in accumulation of toxic chlorinated intermediates and relies on an adequate supply of other organic substrates as electron donors, natural attenuation generally is considered a less favorable remediation technology for chlorinated solvents than for petroleum hydrocarbons (National Research Council, 2000).

Natural attenuation may be a favorable remediation option for chlorinated-solvent ground-water plumes discharging to wetland sediments because the organic-rich nature of wetland sediments and their typically high population density and diversity of microorganisms can enhance biodegradation (Lorah et al., 1997). Under methanogenic conditions, the highly chlorinated solvents have been shown to biodegrade faster and undergo complete dechlorination than under the less reducing conditions of nitrate or sulfate reduction (McCarty and Semprini, 1994; Lorah et al., 1997). Methanogenic conditions are often predominant in freshwater wetland sediments (Capone and Kiene, 1988). In addition to biotic transformations of chlorinated solvents in wetlands, abiotic transformations and physical attenuation processes may be greater than in other ground-water systems (Lorah et al., 1997). Wetlands are extremely important ecosystems, providing habitat for one third of the species listed as threatened or endangered (U.S. Fish and Wildlife Service, 1990). Traditional pump-and-treat remediation and other engineered remediation technologies could destroy some wetland ecosystems by dewatering or

altering ground-water flow. Potentially damaging and costly engineered remedial interventions may be avoided if sufficient natural attenuation of the dissolved chlorinated solvents occurs within the reduced organic carbon-rich wetland sediment zone prior to discharge into the surface water of the wetlands.

A draft protocol for natural attenuation of chlorinated solvents was prepared by the Air Force Center for Environmental Excellence (AFCEE) (Wiedemeier et al., 1996) and later formalized in a USEPA document (Wiedemeier et al., 1998). It was recognized in this protocol that "For sites where contaminated ground water discharges to surface water, the philosophy of monitoring is not well developed." The present document is an addendum to the AFCEE natural attenuation protocol for chlorinated solvents. It does not supersede that protocol, but rather enhances its implementation with respect to wetlands and seeps/springs. This protocol addendum was developed as part of an ESTCP (Environmental Security Technology Certification Program) study of natural attenuation of chlorinated solvents in wetlands. Much of the information presented was gathered from experience gained during the ESTCP investigation at three sites (a freshwater tidal wetland along the West Branch Canal Creek, Aberdeen Proving Ground, MD; a forested swamp in the Colliers Mills Wildlife Management Area at McGuire Air Force Base, NJ; and a seep/spring wetland at Hill Air Force Base, Utah) and from previous investigation work at the APG wetland site (Lorah et al., 1997; Lorah and Olsen, 1999a, b).

The same fundamental principles of the AFCEE protocol hold in the case of wetlands. The main differences lie in the development of a site conceptual model and in the appropriate field methodologies for characterizing natural attenuation processes. Because natural attenuation tends to occur in wetlands at a much smaller spatial scale, site characterization and monitoring methods require greater spatial resolution. The complex hydrology and logistical difficulties associated with most wetland work also require special consideration in selection of field methodologies. The technical methodologies included in this natural attenuation protocol for wetland discharges include collection of soil/sediment borings, reconnaissance methods and strategies, installation of multi-level piezometer (or ground-water sampler) transects, and characterization of the hydrogeology and biogeochemistry. Phytoremediation is another mechanism that can be significant in wetlands, but a review of methodologies for this process are beyond the scope of this project. The Ground-Water Remediation Technologies Analysis Center recently has published an overview of phytoremediation technology (Schnoor, 2002). The protocol presented here is intended to be a guide and not a firm, inflexible procedure to follow. Each site will be unique and discernment must be given as to which methodologies may be most appropriate.

The central elements involved in the consideration of natural attenuation as a remedial action include: (1) determination and documentation of operational natural attenuation processes; and (2) assessment of the level or extent of natural attenuation taking place, as well as its potential for future occurrence, relative to action levels. The National Research Council (2000) lists three basic steps in documenting natural attenuation for ground-water remediation: **"1. Develop a conceptual model of the site:** The model should show where and how fast the groundwater flows, where the contaminants are located and at what concentrations, and which types of natural attenuation processes could theoretically affect the contaminants. **2. Analyze site measurements:** Samples of groundwater should be analyzed chemically to look for footprints of the natural attenuation processes and to determine whether natural attenuation processes are sufficient to control the contamination. **3. Monitor the site:** The site should be monitored until regulatory requirements are achieved to ensure that documented attenuation processes continue



to occur.” “Footprints” are concentrations of reactants or products of biogeochemical processes that transform or immobilize contaminants. This protocol addresses development of a site conceptual model for wetland environments and specific considerations for collecting and analyzing measurements at wetland sites.

## **4.2 Initial Conceptual Model and Site Screening**

The main objective of a natural attenuation investigation is to determine whether regulatory criteria (standards) are met by natural means before receptor exposure pathways are completed. In making this assessment, projections in the extent and magnitude of the contaminant plume in time and space are required. The steps involved in a natural attenuation demonstration, as outlined in Wiedemeier et al. (1996), are given schematically in Figure 4.1. The first step is to review the available site data and determine the present extent of contamination. The site data is used to construct a preliminary conceptual model of the site with particular emphasis on the possible operational natural attenuation processes. An initial screening process (Figure 4.2) is applied to assess the potential of natural attenuation. If data is insufficient to adequately apply the screening process, additional data is collected. Although the general steps for a natural attenuation assessment of a plume discharging to a wetland area are the same as outlined by Wiedemeier et al. (1996), development of a conceptual model and the initial screening process (Figure 4.2) would differ for the case of a suspected discharging plume.

Development of a site conceptual model includes a review of all available information regarding the nature, sources, extent, and magnitude of the contamination; ground-water flow and solute transport; zones where natural attenuation processes may be operational; and locations of potential receptor exposure endpoints. Review of existing classification systems for wetlands and associated theory can be helpful in developing a site conceptual model. A popular hydrogeomorphic approach of wetlands classifies wetlands according to the location of the wetland in the landscape and the dominant sources of water for the wetland (Figure 4.3) (Brinson, 1993; Richardson 1999; Cole and Brooks, 2000). A similar approach to classifying wetland function considers hydrogeologic setting and climate (Winter, 1992; Winter, 2001; Winter et al., 2001). A generic wetland conceptual model for marshes and swamps is given in Figure 4.4 to help in conceptual model development. A similar conceptual model for seep/spring-type wetlands is given in Figure 4.5. For wetlands, attention should be placed on data addressing the following questions: 1) is it a ground-water discharge wetland (as opposed to being primarily recharged with surface water)? 2) is the plume entering into the wetland system (includes the sediment zone)? and 3) in the case of a seep/spring, is the plume truncating in the vicinity of the seep/spring area? If available site assessment data is insufficient to clearly indicate that the plume discharges to the wetland, traditional ground-water data collection is required to delineate the approximate boundaries of the plume from the contaminant source area to the wetland boundary. If the contaminant plume does not currently discharge to the wetland, it should be determined if the plume may reach in the wetland in the future, or if natural attenuation processes within the aquifer upgradient of the wetland are sufficient to lower contaminant concentrations to regulatory criteria before the wetland boundary.

There are sufficient differences between natural attenuation processes in aquifers versus wetland discharges to warrant variations in the initial screening process approach from that of Wiedemeier et al. (1996) (Figure 4.2). A modified initial screening flowchart for wetlands is presented in Figure 4.6. A key change in the initial screening process is that it has to be determined whether ground water is discharging at the wetland, as opposed to a ground-water recharge wetland. If ground water is not discharging through the wetland, natural attenuation within the wetland will not occur and other options should be sought. Often surface features, such as whether the wetland is at the headwaters of a stream, can give an indication that the wetland is fed by ground water. Head distributions provide more concrete indications as to ground-water-flow directions. It is likely to be a "ground-water discharge" wetland if: 1) surficial aquifer heads adjacent to the wetland are higher than the water level in the wetland; and/or 2) heads within the aquifer beneath the wetland become greater with increasing depth (i.e., upward vertical gradient). The first decision loop the screening process for wetland assessments (Figure 4.6) involves determination of ground-water-flow direction in the wetland vicinity. A positive response to the ground-water discharge wetland determination moves the initial screening to an evaluation of natural attenuation potential at the site (Figure 4.6). Another difference in the wetland screening flowchart (Figure 4.6) compared to the Wiedemeier et al. (1996) protocol (Figure 4.2) is that the specific mention of only assessing biodegradation rates to consider the feasibility of natural attenuation has been removed. Other natural attenuation processes in addition to biodegradation are likely to occur in wetland environments. For example, phytoremediation may be the dominant natural attenuation process in seep/spring wetlands. In this case, it would be more important to estimate hydraulic plume capture efficiency (ability of the 'pumping' action of the plants to control the plume) than biodegradation rates.

It should be noted that the initial screening process presented by Wiedemeier et al. (1996) (Figure 4.2) contains a "scoring system" that is not used in this protocol addendum (Figure 4.6). The National Research Council (2000) recommended elimination of the use of "scoring systems" for making decisions regarding natural attenuation because they tend to be too simplistic to represent the complex and site-specific processes involved in natural attenuation. It was recommended that the scoring systems be replaced by evaluation methods using conceptual models and biogeochemical "footprints" (concentrations of reactants or products of biogeochemical processes that transform or immobilize contaminants).

There also are differences in the data collection requirements to assess both subsurface hydrogeology and geochemistry (which reflects biological activity) in a wetland. Since data already exists prior to the wetland, the additional data requirements are focused on locations within the wetland itself. Using the generic conceptual model of a ground-water contaminant plume discharging into a wetland (Figure 4.4), additional data collection locations for screening are schematically shown in Figure 4.7. Multiple sampling locations are needed in the vertical direction because ground-water-flow directions may be predominantly vertical in a discharge wetland. The multi-level sampling transect approach is crucial in the evaluation of natural attenuation in wetlands. Refer to the following section for descriptions of appropriate field methods for monitoring system installation and sampling. In addition to ground-water sample locations for hydrogeological and geochemical data, soil boring information within the wetland is needed during the initial screening process. Two or more soil borings along the transect within the wetland would provide valuable information regarding subsurface features, particularly: 1) the amount of natural organic carbon matter in the wetland sediments; 2)

thickness of the organic carbon zone; 3) qualitative evaluation of the redox status of the wetland sediment by visual inspection and odor (for example, a "rotten egg" odor indicates presence of sulfide); and 4) lithology of the wetland sediment and underlying aquifer, including the presence of clay lenses or low conductivity zones. Refer to the following section for descriptions of appropriate field methods for monitoring system installation and sampling and soil boring collection.

As seen in Figure 4.7, there is an increase in data collection location requirements (about 18 locations versus about 6) over that of Wiedemeier et al. (1996). This can significantly increase sample analysis costs if all analytes proposed by Wiedemeier et al. (1996) are chosen for analysis. An abbreviated list of analytical parameters for screening purposes can focus on those that are most relevant to the assessment of biodegradation within a wetland system, increasing cost-effectiveness: 1) volatile chlorinated organics (parent chlorinated compounds and daughter products), 2) ferrous iron, 3) sulfide, and 4) methane. The strongest evidence to assess natural attenuation is from the spatial distribution of parent and daughter compounds. The decrease of parent chlorinated compound concentrations along the vertical flowpath in conjunction with the production of daughter products is the strongest indication of biodegradation. The other parameters help to confirm whether the conditions conducive to those biological transformations also exist, providing indirect evidence in support of natural attenuation assessment.

If the outcome of the initial screening process (Figure 4.6) yields an affirmative answer, the next phase in the assessment of natural attenuation at the wetland site is to more fully characterize the site to evaluate natural attenuation as a remedial option. This is a phased approach where the results of the initial site screening need to be taken into account in planning and carrying out of the full site characterization. This protocol addendum more closely adheres to Wiedemeier et al. (1996) at this stage by returning to the process flow chart in Figure 4.1. The main addition for characterization of wetland systems is the high spatial resolution required in sampling and monitoring because of vertical ground-water-flow directions and potentially rapid transformations over shorter distances than normally occurs in aquifers (Lorah et al., 1997; Lorah and Olsen 1999a, b; Dyer et al., 2002). Increased temporal sampling also may be required to characterize natural attenuation processes because shallow wetland systems are more effected by seasonal hydrology, temperature, and vegetation changes than deeper aquifer systems (Lorah et al., 2002; Lorah et al., in press).

## **4.3 Field Investigation Methodologies to Support Characterization of Natural Attenuation in Wetlands**

### **4.3.1 Soil/Sediment Boring Collection**

Previous site investigations indicating that a chlorinated solvent plume is heading towards a wetland generally will include soil boring logs that give valuable information on the subsurface geology in the area upland of the wetland. The chlorinated solvent natural attenuation protocol (Wiedemeier et al., 1996) provides information on traditional drilling methods (for example, hollow-stem augur drilling) and direct push methods (for example, GeoProbe) for obtaining subsurface soil samples in the upland areas. Large drill rigs generally are not practical within the wetland area itself due to access difficulties and excessive disturbance of sensitive wetland habitat. It is important to gain stratigraphic information within the wetland itself. Of particular importance are the thickness and nature of the wetland sediments (e.g., organic carbon content), and the nature of the material beneath the wetland sediments including dominant water bearing units and low conductivity units. Selection of soil boring methods within the wetland area is highly dependent upon the site-specific characteristics of the wetland. Small all-terrain vehicles with direct push capabilities may be appropriate at some sites. Other sites with more limited access may require boring methods that are more portable. Innovation and creativity may be required for sediment/soil boring collection within wetlands. Below are potential alternatives.

#### **4.3.1.1 Tripod and Hammer to Drive Split-Spoon**

Split-spoon core samples can be obtained at difficult access locations in wetlands using tripod and hammer devices that can be assembled at the sampling location. Sediment cores were collected at the Aberdeen Proving Grounds, MD West Branch Canal Creek wetland site (Lorah et al., 1997) using a 4.6-m-high tripod equipped with a motorized (5-horsepower) cathead to operate a pulley attached to a 150-pound hammer (see Figure 4.8). The tripod equipment was used to hammer 1.5-m lengths of 0.1-m-diameter PVC casing into the wetland and aquifer sediments. Cores were obtained through the PVC casing using a 0.61-m-long split-spoon sampler attached to 0.073-m-diameter drill rods. In the sand aquifer, sediment was prevented from filling the casing by pumping water from an approved water source through the 0.073-m-diameter drill rods set at depth within the drive casing. Sediment cores were collected until the lower clayey unit was reached at a depth of about 36 m below land surface.

#### **4.3.1.2 Vibracore**

Vibracore technology uses vibration to reduce the drive casing into the subsurface. It is a frequently used technique for obtaining cores in shallow marine or lake sediments. Vibracore systems do not require mounting on vehicles, although that is sometimes done. One of the main advantages of the vibracore systems for use in wetland environments is that they can be disassembled into parts that can be taken to the sampling location, thus allowing access to sites that are difficult to reach and causing minimal disturbance to sensitive habitat.

There are a number of "vibracore systems" available. Some are hydraulic controlled with only vibration, and some are hydraulic controlled with vibration and a hammering action (Figure

4.9). Others have a gasoline engine power source that connects to a vibration unit (either as a vibrator head on top of the casing or as a unit that is clamped onto the side of the casing) by a vibrator cable (much like a speedometer cable). Steel or aluminum casings with a diameter of 0.076 m can be used. A core sample retainer is used to keep the core within the casing during withdrawal. Withdrawal can be accomplished by either a hydraulic unit (if the hydraulic vibracore systems are used) or by winch and a tripod.

A unique application of a vibracore system has been developed by the U.S. Geological Survey in cooperation with Hovertechnics, Inc. of Benton Harbor, Michigan, and MPI Drilling, Inc. of Picton, Ontario (Phelan et al., 2000). A hydraulic vibracore system was mounted on a small hovercraft, creating a "hoverprobe" that can be used for drilling and ground-water sampling in locations accessible to a hovercraft (Figure 4.9c). Hovercrafts can be flown on land, water, mud, snow, or ice, and are propelled by one or more fans that provide both lift and thrust. A scoop behind the fan diverts part of the air under the craft to provide the lift. A rubber-coated segmented skirt surrounds the base of the craft, trapping most of the pressurized air and allowing a constant ground clearance between the craft and the surface. The segmented skirt conforms to various surface textures and conditions, allowing the hovercraft to fly directly between land, water, ice, snow, or mud (Phelan et al., 2000). The drill rig on the USGS hoverprobe is a "Metaprobe" vibracore drill, which is manufactured by MPI Drilling, Inc. Hydraulically driven cams are used to generate high frequency vibrations at the cutting edge of a hollow drill string. A hole and core can be cut, or a monitoring well installed rapidly, with almost no cuttings resulting at the surface. The drill can be used to retrieve continuous core up to a maximum depth of about 100 ft from saturated, unconsolidated materials. The hoverprobe was used to obtain ground-water and lithologic samples to depths of about 15 m along a tidal creek at Aberdeen Proving Ground, Maryland, with drilling continuing as tides changed surface-water levels (Phelan et al., 2000).

#### **4.3.1.3 Direct Push Devices on All-Terrain Vehicles**

A number of drilling firms have mounted direct push rigs such as GeoProbes on various all-terrain vehicles. Obtaining soil borings from moderate depths (less than about 15 m) has become standard practice for GeoProbe-type rigs. A John Deere Gator-mounted GeoProbe was used at a McGuire Air Force Base wetland site that is located in a protected area of the New Jersey Pine Barrens (Colliers Mills Wildlife Management Area) (Figure 4.10). The narrow width (1.5 m) of the Gator allowed access to some sites without cutting trees. The use of the Gator-mounted GeoProbe, however, is limited to wetlands that do not have a large amount of standing water and have relatively level surfaces to drive on. Vertical clearance was found to be a difficulty at the Colliers Mills wetland site due to a highly irregular surface caused by roots and shrubbery.

#### **4.3.1.4 Hand Auger**

Hand augers can be used to obtain disturbed core material to gain information on shallow subsurface geologic conditions. The use of hand augers can be convenient in some wetland environments because it is very portable. One of the difficulties with hand auguring in wetlands is that the borehole may collapse when sampling below the water table. A possible remedy is to drive a PVC pipe with an inside diameter slightly larger than the hand auger outside diameter

into the borehole to keep it open. This will cause some mixing of subsurface materials, so care must be taken in interpreting the soil type from the material in each auger bucket load. The material at the bottom of the auger bucket should be most representative of the material at depth.

#### **4.3.1.5 Shallow Wetland Sediment Coring Devices**

Although mechanical coring devices are needed to obtain deeper sediment samples, these devices typically give poor recovery of organic-rich wetland soils or greatly compact them. Many different types of samplers have been described in the literature for hand-operated sampling of organic-rich soils at shallow depths (generally less than 2.5 m). Landva et al. (1983) and Sheppard et al. (1993) review many of these samplers, giving details of their design, operation, and suitability for accomplishing different objectives. The selection of a soil sampler will vary with the wetland sediment characteristics of a particular site and the purpose for which the sediment sample is needed. Many samplers can be made relatively easily from inexpensive materials. For example, in soft, freshwater marsh sediment at Aberdeen Proving Ground, Maryland, 1.5-m-long section of 0.10-m-diameter PVC pipe that had been sharpened and beveled at one end was used to obtain sediment cores that had been minimally disturbed (Daniel J. Phelan, U.S. Geological Survey, Baltimore, Maryland, oral commun.). An acetate liner was placed inside the PVC pipe, and a well cap that had a small hole in it was placed over the top of the pipe while it was manually pushed into the sediment with a twisting motion. Once the desired depth was reached, the well cap was replaced with one that did not contain a hole and the pipe was pulled upward with wrenches. The vacuum was sufficient to keep the sediment inside the pipe. Recovery was 100 percent using this method in marsh sediment that had some clay content near the bottom. The acetate liner could be gripped with pliers and slid from the pipe, allowing the sediment core to be removed without using a plunger, which can greatly disturb soft sediment. During insertion of a sediment sampling device in organic-rich sediments, compaction as great as 50 percent is a common problem and must be accounted for by measuring depths from the top of the corer to soil on both the inside and outside of the pipe.

#### **4.3.2 Reconnaissance Methods and Strategies**

The preliminary site conceptual model and initial screening process (Figure 4.6) form the basis for reconnaissance strategy and activities. The conceptual model should include presumed contaminant source area, status of that source area relative to contaminant ground-water plume, ground-water flowpaths, approximate location of contaminant plume in aquifer upgradient of the wetland, location of wetland, ground-water flowpaths in wetland, natural attenuation processes that may be occurring in the aquifer, and natural attenuation processes that may be occurring in the wetland (in wetland sediments, plants, and surface water). Site reconnaissance activities should not be designed to provide a full assessment of operational natural attenuation processes at the site, but rather to test principal aspects of the preliminary site conceptual model and to determine whether an adequate natural attenuation "footprint" (National Research Council, 2000) exists to support further assessment of natural attenuation as a remediation option (Figure 4.1 flowchart). The critical first step in the initial screening process (Figure 4.6) is to determine if ground water is discharging into the wetland. Some direct and indirect methods for determining whether the wetland is a ground-water discharge wetland are given in the section



Indicators of Ground-water Discharge Areas below. Other sections describe relatively rapid and inexpensive methods of sampling different media, including surface water, ground water, and trees, to obtain a preliminary estimate of areas of contaminated ground water within the wetland and to guide placement of the final monitoring and assessment network.

The nature of a reconnaissance effort is dynamic in the sense that the presence of parent chlorinated volatile organic compounds (VOCs) and potential daughter compounds can govern the direction of the reconnaissance activity. A local environmental analytical laboratory capable of overnight sample turn-around or on-site chlorinated VOC screening are two ways of providing rapid analytical results and, thus, a dynamic reconnaissance process. If rapid chlorinated VOC analysis is not included at this stage, multiple mobilizations may be required, adding substantially to the cost of the reconnaissance activity. Aspects of on-site VOC analysis are given in the section on on-site chlorinated volatile organic compound screening.

Wetlands often have thick vegetation, and access pathways within the wetland may need to be cleared to begin reconnaissance sampling activities. Access pathways also are important in minimizing disturbance to the wetland ecosystem (field workers should remain on access pathways to the greatest extent possible). Selective cutting or pruning of shrubbery, grasses or marsh reeds may be necessary to create access pathways. This type of disturbance is general short term due to rapid re-growth of vegetation in wetland systems. If standing water or soft sediment is present, temporary wood planking or other materials may be necessary in sampling areas to facilitate sample collection. Access pathways can be marked with highly visible fluorescent plastic survey tape. A small hand-held global positioning system (GPS) can be useful in rapidly determining site location – often with 3 m. Otherwise, compass and field measurement tape can be used to determine approximate sample locations for the purpose plotting locations on a site map during reconnaissance. Surveying of sample locations and piezometers and land surface elevations generally would not be conducted as part of the reconnaissance phase, but after most of the piezometers have been installed for the full natural attenuation assessment phase.

#### **4.3.2.1 Indicators of Ground-Water Discharge Areas**

Determination of areas of ground-water discharge within wetlands, both to the wetland surface and to surface water bodies if they are present in the wetlands, is critical for mapping the contaminant plume and evaluating natural attenuation in wetland sediments. Areas of ground-water discharge can be highly variable spatially in wetland systems. Indicators of ground-water discharge, including physical, chemical, and biological methods, are extremely useful as reconnaissance tools for locating specific sites where detailed measurements and sampling can be focused, helping to guide the monitoring network design in a cost- and time-efficient manner. This section considers possible qualitative indicators or indirect measurements of ground water and/or contaminant discharge, and quantitative measures of ground water and contaminant discharge believed to be most useful for the reconnaissance phase of a study. USEPA (2000) also provides listings and brief summaries of qualitative and quantitative measures of ground-water discharge, along with some extended abstracts and case studies. Selection of a specific reconnaissance method requires consideration of site-specific logistical, physical, and chemical

characteristics. For tidal areas, ground-water discharge areas are best observed or measured at low tide.

Common indirect or qualitative indicators include observations of seeps and springs, thermal infrared mapping, drag probes for temperature, conductivity, or gamma anomalies, and plant distributions. In some settings where flow rates are high, seeps and springs may be observed easily by walking the field area. Water or sediment color and odor sometimes may assist in observing seeps and springs. For example, chemical constituents such as iron and manganese that are dissolved in anoxic ground water precipitate upon contact with oxygenated surface water, causing formation of colored oxides. If the contaminated ground water has a distinct odor, odor could assist in locating ground-water discharge areas. Seeps also may be located by walking an area during colder seasons where ground-water, surface-water and air temperatures are considerably different, causing water vapor or melted ice areas to be visible above seeps.

Temperature measured with thermal infrared imagery also has been used as a reconnaissance tool for finding areas of ground-water discharge to lakes, streams and wetlands (Lee and Tracey, 1984; Silliman and Booth, 1993; Banks et al., 1996; Rosenberry et al., 2000). Airborne thermal-infrared imaging, which measures the relative differences in radiant thermal energy emitted from various earth features, would be most time- and cost-effective for relatively large wetland systems, where the benefits of narrowing the areas needing detailed *in situ* measurements would be greatest. This technique is most likely to be successful in temperate climates during colder months, when high temperature differences would be expected between surface water and ground water and when vegetation growth (which can obscure line of site contact with the land surface) is at a minimum (Banks et al., 1996). Predawn flights in early March were most successful for delineating ground water discharge areas using a thermal-infrared-multispectral scanner at Aberdeen Proving Ground, Maryland (Banks et al., 1996). Banks et al. (1996) were able to distinguish between two types of ground-water discharge—(1) diffuse discharge, which was seen in the estuaries as a pattern of water that grades to cooler water in an offshore direction, and (2) concentrated discharge, which was present in isolated or restricted surface-water bodies and was seen as surface-water temperatures that were similar to the ambient ground-water temperature. Newer high-resolution digital infrared thermography has increased the accuracy of this technique. Airborne thermal infrared imaging can be followed up by ground view thermal infrared video camera sweeps to identify discharge areas on a smaller scale. In larger river or estuarine systems, drag probes that measure temperature and conductivity also may be useful for locating ground-water discharge areas (U.S. Environmental Protection Agency, 2000; Lee, 1985). Dense submerged vegetation, however, can interfere with the performance of this towing method, and it is relatively time-consuming (Rosenberry et al., 2000).

Distribution of aquatic plants have also been used as indicators of ground-water discharge areas in wetlands (Rosenberry et al., 2000; U.S. Environmental Protection Agency, 2000). For example, the distribution of cattail clumps (*Typha latifolia* L.) has been recognized as a fairly reliable indicator of discharge areas of lower salinity ground water in highly saline wetlands (Swanson et al., 1984), and the distribution of marsh marigold (*Caltha palustris* L.) has been used to map seeps and springs next to a lake and in wetlands in Minnesota (Rosenberry et al., 2000). Marsh marigold favors ground-water discharge areas across the upper Midwest states and south central Canada (Rosenberry et al., 2000). This plant has been shown to be a valid indicator of discharge areas in the northern extent of its range (Rosenberry et al., 2000) but not along the southern margins of its distribution across the United States (Carpenter, 1995; Pearson and



Leoschke, 1992). Goslee et al. (1997) describe numerous other plant species that are indicators of ground-water discharge in other locations, and Klijn and Witte (1999) discuss the relation between plants and ground-water flow.

There are many possible direct chemical and physical measurements (for example, specific conductance, temperature, electrical resistivity) that can be made of shallow ground water and surface water to assist in locating plume discharge areas (U.S. Environmental Protection Agency, 2000). However, if a site is contaminated, direct measurement of VOCs probably is best logistically once you have accessed a site. A combination of VOC analyses and head measurements, which can be done with mini-piezometers, provide even more information. Different hand-driven minipiezometer devices have been used successfully for decades to measure the direction of seepage into a surface-water body and head differences between the surface water and ground water (Lee and Cherry, 1978; Woessner and Sullivan, 1984; and Winter et al., 1988). These devices consist of a small-diameter tube (plastic or steel) with a perforated or screened tip inserted by hand in streambed sediment. A small-diameter tube is essential to allow minimum disturbance of the sediment during insertion and minimum lag times to reach hydrostatic equilibrium (Winter et al., 1988). To obtain a direct measurement of hydraulic head difference between surface water and ground water, a manometer can be attached with flexible tubes that extend to the inserted minipiezometer and to the surface water. Head differences can also be determined simply by measuring the level of ground water in the well and level of the surface water outside the well, but the use of a manometer can provide better accuracy and better indication of when hydraulic equilibrium is reached in the inserted minipiezometer. Winter et al. (1988) termed the combination of a minipiezometer and a manometer a "hydraulic potentiomanometer" and describe their design and method in detail. Potential problems that can be encountered also are described, including difficulties in fine-grained organic-rich sediment from clogging of the minipiezometer screen, slow hydraulic equilibrium, or interference from gas release from the sediment (Winter et al., 1988). Ground-water samples for analyses of VOCs also can be obtained from minipiezometers or hydraulic potentiomanometers.

#### **4.3.2.2 On-Site Chlorinated Volatile Organic Compound Screening**

A dynamic reconnaissance effort, where the detection of VOCs in initial samples guides the placement of the following reconnaissance sample locations, is most efficient and informative. Because remobilization costs to a field site can be substantial, it could be cost-effective to have on-site analysis of chlorinated VOCs during the reconnaissance phase. On-site analytical services are readily available by a number of firms. On-site analyses will not comply with certified contract laboratory standards, so it may be necessary to send some duplicate samples to an appropriate certified laboratory. Aqueous sample detection limits in the low micrograms per liter range and compound-specific determinations are required for the chlorinated VOCs. The most common on-site analytical procedures will likely involve gas chromatography, with analytical times of approximately 15 to 30 minutes per sample. Another suitable on-site compound-specific analysis option for aqueous samples is direct-sampling ion-trap mass spectrometry (DSITMS), which does not require compound separation by gas chromatography (Wise and Guerin, 1997). DSITMS gives rapid sample analysis times (less than 5 minutes per sample) that can be advantageous when multiple field teams are collecting samples simultaneously. On-site analysis with DSITMS was used with considerable success in the

reconnaissance phase of the natural attenuation assessment of a TCE plume at the McGuire Air Force Base, NJ wetland site (Colliers Mills Wildlife Management Area).

#### **4.3.2.3 Tree Core Survey**

The analysis of tree cores can be used to delineate shallow ground-water contamination by chlorinated VOCs because these moderately hydrophobic compounds can readily enter trees during transpiration (Vroblesky et al., 1999). If trees are present along the edge or, especially within the wetland, they may be uptaking shallow ground water containing chlorinated VOCs. The sampling, extraction, and analysis of tree core samples is relatively easy, rapid, and inexpensive. Procedures for tree core sampling and analysis can be found in Vroblesky et al. (1999). Because different trees have different uptake rates and root depths that can alter the observed concentrations in the tree cores, it is important to use a single tree species of approximately the same size and to collect the core sample from the same height of each tree. A different extraction and analysis method from Vroblesky et al. (1999) gave good results in the wetland study at McGuire Air Force Base, NJ (Colliers Mills Wildlife Management Area) (Figure 4.11). In this method, the tree core is extracted in 10 mL methanol for a minimum of 12 hr. A second core is taken and put into a vial for later determination of water content. 1 mL of the methanol extract is then diluted in a 40 mL VOC vial with water. The tree core extract then can be analyzed as if it was an aqueous sample (e.g., purge-and-trap GC), and can be done in an on-site or fixed laboratory. If water samples also are being analyzed in the field, this method may be easier to use than the gas analyses detailed by Vroblesky et al. (1999).

Obtaining tree cores and analyzing them for chlorinated VOCs can provide a rapid and cost-effective means to assess chlorinated VOC distributions in shallow ground water. If trees are within the wetland, wide site coverage is possible. If trees are present only along the wetland edge, a tree core survey will provide information only as to the shallow ground-water chlorinated VOC distribution along the wetland edge. If upward ground-water discharge is minimal at the wetland edge and the VOC plume is at some depth in the aquifer, a tree core survey along the wetland edge may give negative results. This was the case at the McGuire Air Force Base, NJ wetland site—tree cores along the wetland edge did not have detectable VOCs whereas those within the wetland where head gradients did have detectable VOCs. Driving and developing piezometers is a more labor-intensive (thus more costly) activity than obtaining tree cores, and a tree core survey may assist in placement of piezometers. Thus, if a tree core survey is to be conducted at the site, it is useful to conduct it early in the reconnaissance phase. A second benefit of a tree core survey is to provide information regarding the potential for phytoremediation at the site.

#### **4.3.2.4 Surface-Water Sampling**

A good description of surface-water sampling methodologies is presented in Appendix A-5 of the Wiedemeier et al. (1998) chlorinated solvent natural attenuation protocol. It is important to note that surface-water samples should be obtained as close to the sediment/water interface as possible since surface-water advection carries water downstream and volatilization will occur at the atmosphere/water interface. The easiest way to collect surface-water samples near the bottom sediment in shallow streams is to simply submerge the sampling container and uncup and fill it at depth. Peristaltic pumps could be used if needed. Surface-water samples can be very

important because surface-water bodies, which can be viewed as receptor endpoints, are often the areas of greatest regulatory concern. During a reconnaissance activity, surface-water samples generally are easy to obtain because surface water in most wetland sites is relatively shallow.

Due to dilution and transport of ground water that is discharged into a surface water body, it also is important to attempt to get sediment pore water samples prior to discharge. There are two easy ways obtaining sediment pore water samples in surface water bodies: 1) hand-installed drive-point minipiezometers; and 2) passive diffusion samplers. The minipiezometers can be pushed easily to shallow depths (less than about 1.5 m) in soft sediments, and may be more convenient than passive diffusion samplers if they purge and recharge rapidly enough for pore water samples to be obtained during the initial visit to the sample location. Passive diffusion samplers made of polyethylene bags filled with VOC-free deionized water (Vroblesky, 2001) can be buried in the shallow sediment for approximately 2 weeks, at which point chlorinated VOC concentrations inside the bag are essentially identical as those in the surrounding pore water. A potential disadvantage of the passive diffusion sampler approach for a reconnaissance activity is the time required to establish equilibrium.

#### **4.3.2.5 Direct Push Piezometers**

The reconnaissance sampling activities in the preceding sections should help delineate the areal extent of the plume, narrowing the area where piezometers need to be installed. Installation of piezometers is needed to obtain water levels to determine ground-water-flow directions and to better define the plume extent. The goals of reconnaissance phase piezometer installation should include determining a major flowpath in the aquifer and wetland sediments near the core of the contaminant plume through the wetland area. A variety of direct push piezometers are available commercially. Care should be taken to insure sample integrity and prevent blockage of intake screen or slots during installation. For shallow applications (depths of less than 1.5 m) in soft wetland sediment, narrow diameter PVC minipiezometers with slotted drive-point tips can be used. The PVC drive point minipiezometers can be installed by hand insertion. For deeper depths, narrow diameter piezometers with stainless-steel drive-point tips with screens are available. With some drive point piezometers (Solinst Canada Ltd., Ontario), Teflon tubing can be connected to the stainless-steel drive point at the top of the screened interval, helping to maintain sample integrity. Drive points with a stainless-steel sacrificial sleeve also are available to protect the screen from getting clogged during installation. When the drive point is driven to depth it is pulled up about 2.5 cm to separate the stainless-steel protective sleeve from the body of the drive point, exposing the inlet screens to formation water.

Drive-point piezometers can be driven into the subsurface by a number of methods. Geoprobe hydraulic units can be used to install them, although there may be site access constraints (see Section 4.3.1.3). For reconnaissance activities, it may be most appropriate to use more portable methods of drive-point installation. Slide bar hammers can be used in many site locations to install piezometers to depths of about 3 to 4 m. A slide bare adaptor piece is attached to the casing to prevent damage to the casing so that additional casing lengths can be attached. A gasoline-powered percussion hammer (such as a Cobra hammer) also can be used to install drive-point piezometers (Figure 4.12). Using a Cobra percussion hammer, drive-point piezometers as deep as 9.8 m (mostly in sand) were installed at the McGuire Air Force Base, NJ wetland site (Colliers Mills Wildlife Management Area). About 6 m, however, was usually the maximum depth until refusal.

#### 4.3.2.6 Hypothetical Reconnaissance Example

Reconnaissance activities are highly dependent upon site conditions, available site assessment information, and site data required to complete the initial screening process (Figure 4.6). Much thought is required in planning the site reconnaissance activities. The main goals of the reconnaissance activities are to complete the initial site screening process and to provide adequate data to develop a comprehensive plan to assess natural attenuation of the chlorinated solvent plume at the wetland site. Although no two sites are identical and approaches to reconnaissance will be distinctly site-dependent, it may be useful to go through a hypothetical reconnaissance exercise for the purpose of illustrating some potential strategies.

The hypothetical site chosen is a mixture of features of the West Branch Canal Creek, Aberdeen Proving Ground, MD wetland site and the McGuire Air Force Base, NJ Colliers Mills Wildlife Management Area wetland site. Mixing the features of the two sites allows for a wider range of reconnaissance tools to be utilized in the illustration. Although the preliminary site data available prior to reconnaissance and the reconnaissance results presented here are hypothetical, actual site features and some general results are represented in this example. A partial site map of the hypothetical site with TCE ground-water contamination is shown in Figure 4.13. The type of information shown is typical of information gained as a result of a traditional site contaminant assessment. Clusters (3 and 9 m deep) of conventional ground-water monitoring wells were installed only in areas readily accessible by a drill rig (i.e., the edge of the wetland, which is a dense wooded area that has periodic standing water). The piezometric head data indicates ground-water flow is towards the wetland. Boring logs indicate that the shallow aquifer consists of unconsolidated sand and that an aquitard is present at approximately 14 m below ground surface. Historical information indicates that a waste solvent disposal ditch is located approximately 500 m upgradient of the edge of the site map shown. As typical with many TCE source areas, actual dense non-aqueous phase liquid (DNAPL) was not found, although ground-water TCE concentrations strongly suggest that DNAPL is present. Unless the source area is removed or contained, a substantial TCE ground-water plume will likely continue to be generated for many years (possibly decades). This pattern of available site data was observed in many of the sites considered for inclusion in the ESTCP wetland natural attenuation study.

Beyond the wooded area is a heavily vegetated marsh that routinely has shallow standing water. The surface wetland sediment in the marsh appears to have a high organic carbon content and is very dark. In walking through the marsh, a hydrogen sulfide odor is observed, indicating reducing conditions conducive to microbial reductive dechlorination of the chlorinated solvents within the wetland. A creek runs through the marsh. Available information indicates that the creek always contains surface-water flow. The head of the creek is only about 300 m upgradient of the portion of the creek shown on the site map. The close proximity of the head of the creek and the constant flow in the creek provides an indirect indication that shallow ground water should generally be discharging in the wooded and marsh wetland areas, although limited periods of ground-water recharge in the wetland might occur during periods of high rainfall.

The available ground-water monitoring data indicate that the TCE contaminant plume approaching the wetland is some distance beneath the water table (i.e., there is a layer of relatively clean ground water above the plume). This is a common phenomenon in contaminant plumes extending from DNAPL sources in upland recharge areas. Very low 12DCE concentrations and no vinyl chloride is observed, indicating that little natural attenuation due to

reductive dechlorination occurs within the aquifer prior to the wetland. Dissolved oxygen (DO) levels are greater than 2 ppm, further indicating that natural attenuation by anaerobic reductive dechlorination within the aquifer is not occurring to any great extent.

The presence of a wooded wetland area allows the use of a tree core survey to provide a rapid and cost-effective indication of shallow ground-water TCE concentrations over a relatively broad area immediately downgradient of where the TCE plume is known to be. The tree core survey is conducted early in the reconnaissance activity in an attempt to define the area where the TCE plume enters the marsh area. The wooded area contains a mixture of trees, hardwoods, and pines. Pines are chosen for the tree core survey due to their wide distribution and shallow root systems, thus providing a potential indication of relatively shallow TCE ground-water concentrations. The results of the tree core survey for TCE are shown in Figure 4.14. On-site chlorinated VOC screening for the tree core samples is conducted to provide results within one day of sampling. Two parallel transects are made with trees being sampled being about 200 m apart--one transect close to the upgradient edge of the wooded area and the other along the downgradient edge closest to the marsh. The placement of these transects was governed by the previously available site data suggesting that the TCE plume is flowing towards the wetland in this area. The upgradient tree core transect showed mostly non-detectable concentrations, but low TCE concentrations are observed in trees downgradient of MW-12 and MW-13 (12DCE is not observed in the upgradient transect). The downgradient tree core transect shows substantially higher levels of TCE, particularly in the region downgradient of MW-12 and MW-13, while low or non-detectable TCE concentrations are observed at both ends of this transect. Low levels of 12DCE are observed in the tree core data from the downgradient transect. The tree core survey indicates that the core of the TCE ground-water plume continues downgradient of MW-12 and MW-13. The TCE plume appears to be rising vertically along the ground-water flowpath. This is likely due to both the ground-water "pumping" action of the trees and to an upward head gradient within the wooded and marsh portions of the wetland. The 12DCE observed in the downgradient tree transect indicates that some reductive dechlorination may be occurring in the shallow subsurface at that point.

The next phase of the reconnaissance is to collect and analyze creek surface-water samples and shallow creek sediment porewater samples for on-site VOC screening. Samples were collected along the creek at locations about 200 m apart. Sediment porewater samples were collected from a depth of 1 m below land surface using minipiezometers. At each location, surface water and porewater samples were taken at the same time. The TCE and VC results of the surface water and porewater samples are shown in Figures 4.15 and 4.16, respectively.

The results of the surface-water sampling indicate that low levels of TCE are entering the creek. Concentrations were below the 10 ppb TCE drinking water standard, although concentrations may vary with changing hydrogeologic and rainfall conditions. The sediment porewater TCE results indicate that the TCE ground-water plume continues along the presumed ground-water flowpath from MW-12 and MW-13, through the area where the tree core TCE results were highest, and then directly towards the creek. TCE concentrations in the sediment porewater were significantly lower than that observed in MW-12 and MW-13 suggesting that natural attenuation is reducing the TCE concentrations within the plume as it enters the wetland sediment. Although not shown, DCE concentrations in the sediment pore water are generally within a factor of 3 of the TCE concentrations, indicating the reductive dechlorination is occurring. On-site analyses of sediment porewater samples for dissolved oxygen (DO), ferrous iron, and sulfide indicated reducing conditions. Low concentrations of VC are observed in the



porewater samples with the highest TCE concentrations, indicating that reductive dechlorination of TCE is continuing past 12DCE to VC. VC also may be degrading, by either anaerobic reductive dechlorination to ethene or by oxidation. The fate of VC will require additional investigation after the reconnaissance phase.

The downgradient tree transect and creek porewater results suggest that the TCE plume has risen vertically upward as it has moved downgradient. The final part of this reconnaissance is to gain additional confirmation that the TCE plume has risen vertically as it goes through the wetland system and to confirm the main axis of the plume. Drive-point piezometers are installed manually along a transect in the marsh near the downgradient tree core transect. Sample locations are selected judiciously based upon the tree core survey, creek surface water and creek sediment porewater results. Six piezometers are installed in the aquifer to a sampling depth of 3.6 m below land surface. Piezometer locations and ground water TCE concentrations are shown in Figure 4.17. Low 12DCE concentrations and no VC concentrations are observed in the ground water at these piezometers, suggesting little natural attenuation by anaerobic reductive dechlorination in the aquifer. DO levels above 2 ppm in all of the piezometers indicated that aerobic conditions exist. The TCE concentrations confirm the presumed flowpath of the plume. In addition, TCE concentrations in the 3.6 m-deep wetland piezometers are similar to those observed in the 9-m-deep MW-12 and MW-13 wells, indicating upward movement of the plume in the wetland area. The similar TCE concentrations at these upgradient and downgradient locations again suggest that little natural attenuation is occurring in the aquifer.

The net result of this hypothetical reconnaissance is that we are able to confirm that this is a ground-water discharge wetland and that significant natural attenuation processes appear to be occurring within the wetland and creek bottom sediments. These results provide the basis for planning further investigations of the natural attenuation processes occurring at this site. The hypothetical reconnaissance activities described should be able to be conducted in one week with a field team of 4 individuals (field analysis chemist, field team chief, and two field technicians). Note that additional time would be required for mobilization, demobilization, and report preparation.

#### **4.3.3 Multi-Level Transects**

To evaluate the natural attenuation of chlorinated solvents discharging into wetland environments, the biogeochemistry of the ground-water plume as it moves through the wetland needs to be defined. This subsurface biogeochemical information needs to be obtained both vertically and horizontally, requiring multi-level transects of ground-water sampling devices. Installation of traditional ground-water monitoring wells that require large drill rigs are not feasible in most wetland environments due to the wet conditions and the fragile nature of wetlands. Mobile and less intrusive installation methods are required. At most sites, the use of only one ground-water sampling methodology will generally not suffice, since two types of subsurface environments must be sampled: 1) the deeper aquifer beneath the wetland; and 2) the shallower organic-rich wetland sediments. Much of the most valuable biogeochemical information supportive of natural attenuation is gained from the shallower organic-rich wetland sediments that cannot be easily sampled using traditional piezometers. The organic-rich layer of wetland sediments often is thin (less than 2 m), diffusion can be a significant upward transport mechanism of solutes, and steep vertical changes in concentrations can occur. To characterize the biogeochemical reactions in these environments, porewater samples need to be obtained at

closely spaced vertical intervals. Wells and piezometers with 5-cm diameters and screen lengths of 30 cm or more that are used in traditional ground-water investigations may be unsuited for characterization of wetland sediments.

A number of novel ground-water sampling methodologies appropriate for wetland systems are available. Discussed in this section are four methodologies examined in the ESTCP chlorinated solvent wetland study: 1) direct push piezometers that have narrow diameters and short screen lengths; 2) a multi-level monitoring system; 3) tubing samplers; and 4) peepers (a type of passive diffusion samplers). Advantages and disadvantages of each of these methodologies are detailed in Table 4.1. Results of comparison of the four sampling methodologies that was conducted as part of the ESTCP chlorinated solvent wetland study are summarized in Section 4.3.3.5.

Table 4.1. Comparison of Sampling Devices

Sampling Device	Advantages	Disadvantages
Drive-Point Piezometer	<ul style="list-style-type: none"> <li>• Shallow/moderate depth multi-level sampling</li> <li>• Fe results generally similar to peepers</li> <li>• Generally good comparisons to other devices at &gt;100 cm depths</li> <li>• Able to obtain hydraulic parameters</li> <li>• Moderate expense/maintenance</li> <li>• Moderate ease of installation</li> </ul>	<ul style="list-style-type: none"> <li>• VOC concentrations generally lower than peepers</li> <li>• VOCs and redox species subject to aeration at shallow depths</li> <li>• May draw water from other areas during sampling</li> <li>• Can create channeling if well diameter too large or too close</li> <li>• May reflect local spatial heterogeneities because of nest</li> <li>• Slow recovery after purging in wetland sediments</li> </ul>
Tube Sampler	<ul style="list-style-type: none"> <li>• Shallow depth multi-level sampling</li> <li>• Total VOC results similar to peepers</li> <li>• Fe good at depth compared to other devices</li> <li>• Assesses potential impact from macropore flow</li> <li>• Low expense/maintenance</li> <li>• Ease of installation (no drilling)</li> </ul>	<ul style="list-style-type: none"> <li>• Interception of macropore flow may obscure biodegradation reactions occurring in rest of wetland sediments</li> <li>• Difficult to sample because of low well volume</li> <li>• Unable to obtain hydraulic parameters</li> <li>• May reflect local spatial heterogeneities because of nest</li> <li>• Can easily move up or down unless well-anchored at land surface</li> <li>• Slow recovery after purging</li> </ul>
Peeper	<ul style="list-style-type: none"> <li>• Shallow depth multi-level sampling</li> <li>• Gives the best vertical resolution of porewater chemistry</li> <li>• Best indicator of porewater chemistry (highest overall VOC and redox-sensitive concentrations)</li> <li>• Least affected by spatial heterogeneities because of diffusion</li> <li>• Less chance of aeration during sample removal and no recovery time problems</li> <li>• Large number of porewater samples collected simultaneously</li> <li>• Ease of use (no drilling) and inexpensive to install</li> <li>• Mobile, reuseable</li> </ul>	<ul style="list-style-type: none"> <li>• Small sample volume; unable to repeat sampling without reinstalling</li> <li>• Labor intensive/time consuming for preparation</li> <li>• Unable to obtain hydraulic parameters</li> <li>• Difficult to insert/remove in semi-dry or tight sediments, or where tough roots are present</li> <li>• Porous membrane expensive but overall are least expensive in terms of material and installation</li> <li>• Repeated installation and removal at same site disturbs sediment</li> </ul>
Multi-Level Sampler	<ul style="list-style-type: none"> <li>• Shallow/moderate depth multi-level sampling</li> <li>• Methane results similar to, or greater than, peepers</li> <li>• Discrete vertical increments without effects from lateral spatial heterogeneities as may be observed in clustered samplers</li> <li>• Able to obtain hydraulic parameters</li> <li>• Fast recovery after purging</li> <li>• Ease of sampling—7 depths in one borehole</li> </ul>	<ul style="list-style-type: none"> <li>• VOC results lower than other devices at shallower depths</li> <li>• Bentonite and chamber sealants may affect results</li> <li>• Possible problems with inadequate seals between bentonite packs</li> <li>• Possible cross-contamination by diffusion through polyethylene</li> <li>• Drilling equipment required (difficult logistics in wetlands)</li> <li>• High initial cost</li> </ul>



#### 4.3.3.1 Direct Push Piezometers

For most wetland sample locations deeper than 1 m, direct push piezometers may be appropriate. Hardware and supplies for direct push piezometers are available from a number of vendors. Piezometers with maximum diameters of 1.9 cm and maximum screen lengths of 15 cm are most appropriate for characterization of wetland porewater chemistry and hydrology. Larger piezometers may take too long to recover after purging, may respond too slowly to changing hydrologic conditions (such as tidal changes in head), and sample water from too many biogeochemical zones to allow an understanding of degradation processes. The Solinst Canada Ltd. Model 615S shielded drive point piezometers (Figure 4.18) were used for the ESTCP wetland chlorinated solvent natural attenuation study. The shielded drive point is driven to depth and then pulled back about 15 cm to detach the drive-point tip from the screened sample ports (the detachable drive-point tip is attached to the rest of the drive point with a rubber o-ring). This helps to prevent clogging of the sample ports with silt or clay during installation. At one of the ESTCP sites, difficulties were encountered in detaching the drive point and were solved by simply omitting the o-ring. The drive point components (detachable tip and unit with sample ports) are made of stainless steel. The drive point is attached to 1.27-cm outer-diameter Teflon tubing by a tubing barb, so that sampled ground water contacts only the stainless steel and Teflon. The Teflon tubing fits within 1.90-cm diameter steel pipe. Pipe segments are connected with threaded couplers, with heavy-duty couplers (thicker couplers with steel extending beyond the threads for extra support) recommended for greater depths. Drive-point piezometers can be driven into the subsurface using a number of different methods. Some installation methods that use portable hammers or small drilling equipment appropriate for wetland environments were discussed in earlier sections on soil/sediment boring and reconnaissance methods, including vibratory rigs (Figure 4.9), Geoprobe rigs (Figure 4.10), and gasoline-powered percussion hammers (Figure 4.12).

#### 4.3.3.2 Multi-Level Monitoring Systems

Multi-level monitoring systems (MLMS) that typically consist of multiple screened intervals separated by packers are available from several vendors to obtain vertically spaced sampling intervals in a single borehole. In addition, bundle-type multi-level monitoring systems commonly have been constructed by individuals using tubings of varying lengths that are covered at the tips with mesh screens and secured into a bundle that will fit into one borehole (Cherry et al., 1983). Similarly, multi-port samplers that have individual tubes inside an outer casing have been constructed (Delin and Landon, 1996). Bentonite packers above the screens help limit cross-flow between the screened intervals of multi-level or multi-port samplers. Installation of MLMSs generally involves placing it in a cased borehole and then removing the outer casing, relying on collapse of the sediments around the borehole to secure the MLMS and provide a complete seal around the screened intervals. Although this method can work well in unconsolidated sands, clayey wetland sediments might not collapse as easily as sands, potentially leaving channels around the MLMS that connect the screened intervals. Incomplete collapse of wetland sediments was observed at the APG site when hand-made bundle-type piezometers were used in a ground-water tracer test in 1998.

For the ESTCP wetland study, a MLMS that is complete within one single length of tubing was tested. The MLMS from Precision Sampling Inc. (Richmond, California; [www.precisionsampling.com](http://www.precisionsampling.com)) was used in a sampling method comparison study as part of the

ESTCP wetland demonstration. The basis of the Precision Sampling MLMS is a seven-chamber polyethylene tubing unit (called Continuous Multi-Channel Tubing by Precision, Inc.) that is used to make seven discrete sampling levels within a single borehole (Figures 4.19 and 4.20). The seven chambers are arranged in a wagon wheel fashion with six chambers around a single chamber in the middle. The center chamber can only be accessed through the bottom without going through one of the side chambers, so the center chamber is used for the deepest sampling location. The MLMS can be prepared on-site after screen locations are determined. At the bottom of the tubing, the six outer chambers are sealed off using silicone sealant and hot glue. A stainless-steel screen is placed around the bottom and secured in place with stainless-steel wire. For each of the six outer chambers, several sample ports were drilled into the individual channel at the desired depth, creating 7.6-cm-long sampling intervals. Sealant was injected in another hole to create the bottom of the sampling chamber for each sampling level. Stainless-steel mesh and sand packers are secured around each sampling interval with wire. Bentonite packers are placed between each of the sampling intervals and their associated sand packers. As soon as the MLMS is placed to the bottom of the borehole, the outer casing has to be withdrawn rapidly while manually holding the MLMS in position. If the bentonite packers are made too thick and/or the casing is not withdrawn rapidly enough, swelling of the bentonite may cause the MLMS to come out with the casing, making it necessary to repeat fabrication and installation of the MLMS.

#### **4.3.3.3 Tubing Samplers**

A simple method for obtaining closely spaced (centimeter scale) vertical samples needed for multi-level transects in wetland sediments is to use tubing samplers. The tubing samplers that were evaluated as part of the ESTCP chlorinated solvent wetland study is similar to a minipiezometer, except for the inverted screen that is placed pointing upward from the bottom of the tube (Figure 4.21). These tubing samplers originally were fabricated for use in a ground-water-flow tracer test in the wetland sediments at the APG site; piezometers were needed that did not have protruding screens that might cause channeling of flow along the outside of the piezometer casing (a problem that was observed with bundle-type multi-level piezometers in these wetland sediments). The tube samplers were constructed of thick-walled 0.64-cm-diameter stainless-steel tubing. The narrow diameter tubing allows several of these samplers to be placed close together on a horizontal spatial scale, minimizing disturbance of vegetation and minimizing possible spatial heterogeneities across a nest of tube samplers. A conical 7.6-cm-long, 100-mesh stainless-steel screen was inserted tightly into one end of the tube, forming an inverted screen that gives an extremely small discrete sampling interval. To prevent clogging of the screen during insertion, organic-free deionized water was forced into the tube concurrent with its manual insertion into the sediment. To ensure that the thin tubes were installed vertically from the surface and to prevent leaning or horizontal movement once in place, the tubes were inserted through holes that had been drilled into two small untreated plywood platforms, one atop the other. The platforms were anchored to a nearby PVC pipe.

#### **4.3.3.4 Peepers**

Peepers are a type of passive diffusion sampler that originally were designed for obtaining closely spaced (millimeter scale) vertical samples in fine-grained bottom sediments in lakes

without disturbing natural flow (Hesslein, 1976). Diffusion samplers are effective at obtaining samples in sediments where flow velocities are low (about a meter per year or less), and diffusion is a major transport mechanism. Peepers commonly have been used for sampling redox-sensitive constituents and trace metals; the APG wetland study at West Branch Canal Creek first reported use of peepers for sampling of volatile organic contaminants (Lorah et al., 1997; Lorah and Olsen, 1999a, b). A schematic of a typical peeper design is shown in Figure 4.22. Peepers typically are constructed out of acrylic or polycarbonate, and sampling cells are covered with a permeable membrane. For the ESTCP wetland demonstration and previous work at the APG site, 0.2- $\mu$ m filter paper (HT Tuffryn, Pell Corporation, Ann Arbor, Michigan) was used for the permeable membrane. A local plastics manufacturing company machined peepers to our specifications. The bodies of the peepers were constructed from a solid 2.5-cm-thick acrylic plate. Oval chambers were cut completely through the plate to form sample chambers that were spaced 3.0 cm apart for a 60-cm-long peeper and 5.5 cm apart for a 120-cm-long peeper (a total of 21 to 22 rows of sample chambers in each peeper). Two thin acrylic sheets, termed "membrane support plates", were machined in a similar fashion and attached with nylon screws to either side of the thick plate. The membrane support plates hold the permeable membrane (cut to cover the length of the peeper in one piece) over the sampling chambers. A handle was machined into the top of the plate, and the bottom was tapered into a sharp blade for ease of insertion into sediments.

To prepare the peeper for use, a membrane sheet is put between the support plate on one side of the peeper and the Nylon screws are screwed on snugly. The sample chambers then are filled with VOC-free deionized water, overfilling to prevent trapped bubbles, before the second membrane sheet is screwed onto the other side. Because anaerobic subsurface conditions likely exist in organic-rich wetland sediment, it is important not to introduce oxygen into the sediment from the peeper. To remove oxygen within the deionized water in the peeper chambers and oxygen held in pores in the plastic, the peeper should be placed in a container filled with deionized water and sparged with nitrogen gas for at least 12 hr. A large-diameter PVC pipe can be made into a sparging container by sealing a cap onto the bottom of the pipe and making fittings in a top cap to extend a flexible tubing from the gas tank and through the water-filled PVC pipe.

The peeper should be inserted in the sediment immediately after removing the peeper from the sparging container. The peepers can be pushed manually or pounded gently into the sediment (hard pounding can cause deionized water to be lost from the sample chambers and could crack the plastic). Peepers generally are left in the sediment for about 2 weeks to equilibrate before removing them to sample. Webster et al. (1998) discuss equilibration dynamics for peepers and the effect of peeper dimensions and solute diffusivities on equilibration times. Sometimes the peeper can be removed simply by grabbing the handle with a hand and pulling out of the sediment, although a lever device may be needed to assist in removing the peeper (for example, Figure 4.23). Once extracted, one side of the membrane for each sample chamber is pierced one at a time, and sample is removed using syringes with short pieces of soft flexible tubing attached to the tip. Tests performed at the APG wetland site indicated that one peeper can be sampled for VOCs, ferrous iron, sulfide, and methane in about 1 hr and that sample integrity was maintained during this period. The sediment that typically coats the peeper membrane (Figure 4.23) probably assists in slowing oxygen diffusion into the membrane or volatilization of constituents out of the chambers during this period. An anaerobic glove bag can be used if longer sampling times are needed.

#### 4.3.4.5 Comparison of Multilevel Transect Sampling Devices

During the ESTCP wetland study, additional sampling devices were added to six sites where clusters of drive-point piezometers already existed—MLMSs (Precision, Inc.), tubing samplers, and peepers. All the devices at each site were sampled for VOCs, ferrous iron, sulfide, and methane during two events. The different screen sizes of the sampling devices probably account in part for the differences observed in concentrations among the sampling devices. The drive-point piezometers had the longest screened interval (15.2-cm) and thus were most likely to obtain water from a mixture of zones during sampling. The tubing samplers and peepers had the most discrete sampling intervals. Because each peeper provided the most closely spaced sampling points, these gave the greatest vertical resolution of changes in biogeochemical constituents in the wetland porewater, providing the best indication of redox conditions and degradation reactions in the wetland sediment (Figure 4.24). Higher concentrations of ferrous iron, sulfide, and methane generally were observed in the peepers than observed at comparable depths in the other sampling devices. In addition to higher concentrations of the redox-sensitive species, the peepers sometimes showed higher concentrations of daughter VOCs and total VOCs compared to the other devices. These results may be attributed in part to the lower chance of sample aeration and volatilization in the peepers because samples are passively collected, and in part to the peepers measuring constituents transported through the wetland sediments by diffusion where greater biodegradation can occur. Diffusion may be the primary transport mechanism in wetland sediments that have a low permeability. At both the Aberdeen Proving Ground, MD, and McGuire Air Force Base, NJ wetland sites studied during the ESTCP demonstration, peepers were crucial in determining biodegradation efficiency and evaluating seasonal changes in biodegradation in the shallow wetland sediments (Dyer et al., 2002; Lorah et al., 2002).

At depths greater than about 100 cm, concentrations of VOCs and redox-sensitive constituents measured among the MLS, tubing, and piezometers were more consistent than at shallower depths. Drive-point piezometers may be needed to reach deeper depths and to obtain water level measurements, but chemical data for volatile and redox-sensitive constituents obtained from piezometers in shallow anaerobic wetland sediments (less than 100 cm) should be interpreted with caution.

Of the 4 sampling devices used, water levels could be measured only in the drive-point piezometers and MLMSs. Water levels were generally lower in the MLMSs compared to the piezometers at the same depth. The small diameter of the sample chambers in the MLSs apparently causes inaccurate water-level measurements.

Other logistical considerations also are summarized in Table 4.1 for the four sampling devices. For example, the MLMS wells were the most productive of the four devices. The channels were of adequate diameter to hold sufficient ground water for sampling, and because sand packs surround each of the sampling ports, relatively fast recovery occurred during purging. In contrast, the tube samplers delivered the lowest volumes of sample water. Given their small well diameters, it was often difficult to extract the necessary volumes for analysis of all constituents, particularly in the shallower wells. Some tube samplers did not recharge after purging in a timely manner to obtain all of the desired samples. The tube samplers had the advantage of being the least expensive and complicated of the devices to construct and install.

The peeper's mobility is a distinct advantage compared to the other devices; however, repeated installation and removal at a particular site may disturb the sediments.

#### 4.3.4 Characterization of Hydrogeology

Wetland hydrology is complex and poorly understood compared to deeper flow systems. Complicating factors include the high degree of heterogeneity in lithology common in wetland sediments, the complex hydraulic properties of organic-rich soils, and the greater temporal variations (from seasonal recharge changes, tidal effects, evapotranspiration effects, and storm-related effects) in wetlands compared to deeper flow systems (Hunt et al., 1996). Some considerations for characterizing the hydrogeology of wetland sites are discussed here.

Darcy's law commonly is used to calculate ground-water-flow rates, using measured hydraulic heads and estimates of hydraulic conductivity. In wetlands, it is critical to obtain both horizontal and vertical head gradients to calculate horizontal and vertical flow rates. Vertical flow rate may be dominant in much of the wetland. However, calculating vertical flow has a greater uncertainty than horizontal flow calculations, largely because of the greater difficulty in determining vertical hydraulic conductivity (Hunt et al., 1996). Vertical hydraulic conductivity commonly is estimated from the horizontal hydraulic conductivity, because accurate methods of independently determining this term are lacking. The vertical component of hydraulic conductivity can be calculated using the equation (Lee and Fetter, 1994, p. 127-128):

$$K_z = \frac{b}{\sum (b_i/K_i)}$$

where

$K_z$  is the mean vertical hydraulic conductivity ( $LT^{-1}$ );

$b$  is the total length of the flow line (L);

$b_i$  is the length of the  $i^{th}$  increment (L); and

$K_i$  is the horizontal hydraulic conductivity of the  $i^{th}$  increment ( $LT^{-1}$ ).

Horizontal hydraulic conductivities traditionally are measured using pump tests, slug tests, or sieve analysis of sediments (Lorah et al., 1997; Weidemeier et al., 1996). Hydraulic conductivities also can be estimated from the response of water levels in piezometers to cyclic fluctuations from tides or evapotranspiration (Lorah et al., 1997). Pump tests are not appropriate for wetland environments because the large hydraulic stresses associated with prolonged pumping can change pore diameters in organic-rich sediments and cause conductivities to vary over time. A similar problem can occur with slug tests in wetland sediments (Hunt et al., 1996). Hunt et al. (1996) compared flow rates measured in wetland sediments at 3 sites using three independent methods—Darcy's law calculations with horizontal hydraulic conductivity estimated from slug tests, stable isotope mass balance techniques, and temperature profile modeling. The Darcy's law calculations gave lower estimates of flow rates than the other two methods. The results of the stable isotope method and temperature profiling agreed within the same order of magnitude and had smaller uncertainty associated with the results than the Darcy's law calculations. In a study of a fringing wetland in Virginia, Tobias et al. (2001) found that the best method to measure ground-water discharge varied seasonally. The Darcy law method provided the most reliable estimate during low ground-water-flow conditions in the fall, whereas a salt mass balance method provided a better estimated of discharge during high flow conditions



in the spring (Tobias et al., 2001). Ground-water tracer tests with a conservative tracer are another method to obtain ground-water flow rates (Tobias et al., 2001). Despite the uncertainties that may be associated with the Darcy's law method for wetland sediments, this method requires the least manpower and other resources to complete. Because of the spatial heterogeneity common in wetlands, hydraulic conductivity and flow estimates are best estimated for as many different areas of the site as possible. Although a wetland may be predominantly classified as a discharge area, localized recharge areas also can occur in a wetland (Hunt et al., 1996).

Temporal variability in ground-water-flow rates and directions also can be large, requiring semi-continuous or repeated measurements of hydraulic head at time-scales appropriate to assess this variability. Development of a conceptual model of the hydrogeomorphic landscape (Brinson, 1993; Winter, 2001; Winter et al, 2001) of the wetland can assist in determining appropriate scales over which to make hydrologic measurements. For example, if a wetland is thought to derive a large component of its water source from precipitation (Figure 4.3), measurements during rainfall events will assist in evaluating the hydrology and contaminant attenuation processes. At the McGuire Air Force Base, NJ wetland site (Figure 4.3), high periods of recharge resulted in reversals in ground-water flow and a subsequent increase in the oxidation state of the ground water, which caused biodegradation of TCE to decrease (Lorah et al., 2002). At the Aberdeen Proving Ground, MD wetland site (Figure 4.3), tidally induced changes in head cause reversals in ground-water-flow directions at some sites and also result in focused ground-water discharge of contaminants in unexpected areas of the wetland (Lorah et al., 1997; Lorah and Olsen, 1999b).

Ground-water discharge rates to surface-water bodies in the wetland area can be calculated by the same methods as discussed in the section above. In addition, seepage meters commonly have been used to directly measure ground-water discharge rates to surface water, including lakes, streams, and coastal waters (Lee, 1977; Lee and Cherry, 1978; Woessner and Sullivan, 1984; Shaw and Prepas, 1989; Cable et al, 1997). The basic seepage meter consists of the bottom section of a 55-gallon drum or smaller bucket (depending on the area of the study site) and a plastic water collection bag, connected to the bottom of the drum with an open port. The seepage rate is measured from the volume of water that enters the bag over a known time and area. Controlled experiments in tanks have indicated that seepage meters provide reliable measurements, although there was a constant bias in the measurements related to frictional resistance and head losses within the prefilled collection bags (Belanger and Montgomery, 1992; Isiorho and Meyer, 1999). The highly variable seepage measurements that can be found in the field probably are related largely to the spatial variability in hydraulic conductivity (Shaw and Prepas, 1990; Belanger and Montgomery, 1992).

#### **4.3.5 Biogeochemical Characterization**

Characterization of natural attenuation of chlorinated solvents in wetlands requires the same biogeochemical data as outlined by Weidemeier et al. (1996) for other subsurface environments, including parent and possible daughter compound VOCs, constituents that indicate the redox state of the ground water (such as dissolved oxygen, ferrous iron, sulfide, sulfate, nitrate, ammonia, methane, hydrogen), and other water-quality measurements that can provide geochemical "footprints" (National Research Council, 2000). Demonstration of natural attenuation includes demonstrating decreasing contaminant concentrations along ground-water flowpaths or through time from historical data, and linking the decreasing concentrations to

attenuation mechanisms. For assessment of natural attenuation in wetlands, changes in flowpaths and the potentially strong temporal variability in biogeochemical processes must be considered. Changes in concentrations must be evaluated along both horizontal and vertical ground-water flowpaths, requiring multi-level transects and closely spaced sampling intervals in the wetland sediment as previously discussed. To assess historical changes over time in contaminant concentrations in the wetland porewater, historical changes in contaminant concentrations in the aquifer that is transporting the contaminants to the wetland also would need to be known. In addition, seasonal and other temporal effects on contaminant concentrations and attenuation processes would need to be evaluated. For example, 4 years of monitoring at the Aberdeen Proving Ground wetland site have shown an annual cycle of maximum VOC concentrations in the shallow wetland porewater in the late spring and summer and minimum VOC concentrations in the winter and early spring. VOC concentrations in the shallow wetland porewater change by a factor of 3 to 4 in this annual cycle, while concentrations in the underlying aquifer remain approximately the same. These seasonal changes in the wetland contaminant concentrations are believed to be associated with changing hydraulic heads in the aquifer (and thus changes in the flux of VOCs being transported upward to the wetland sediments), rather than with changes in biodegradation or other attenuation processes (Lorah et al., 2002; Lorah et al., in press).

Biogeochemical characterization in wetlands also requires unique consideration of sampling methods. Because of the small-diameter, closely spaced samplers needed for sampling wetland sediments and the generally low permeability of wetland sediments, only low sample volumes generally can be obtained without altering the natural flowpaths and consequently mixing water from different biogeochemical zones. For sampling drive-point piezometers and other devices that do not have a sand pack or other construction materials surrounding the casing, removal of 1 to 2 well volumes generally is sufficient for purging. Only 1 well volume commonly was purged from piezometers screened in the wetland sediment during the ESTCP wetland study because they would become dry. The generally low recovery rate and narrow diameter of the sampling devices in wetland sediments often required a non-traditional sampling method. Piezometers screened in the wetland sediment were purged and sampled with syringes that had tubing extending to the piezometer screen. Gently drawing sample into the syringe after expelling air allows sample to be collected at a low flow rate and with minimum aeration. The use of a 3-way valve between the tubing and syringe allows air from the top of a sample stream to be eliminated before collecting the sample, and shutting the valve to the tube holds the water in the tubing while the syringe is removed to expel sample into a bottle.

Because these piezometers and the peepers give limited sample volumes, not all analytes recommended by Weidemeier et al. (1996) can be measured. Available site data and preliminary tests of the water could be used to decide on the critical parameters needed for a specific site. For example, available data on the low nitrate concentrations in the aquifer and in initial tests of the wetland porewater were used to eliminate nitrate and ammonia from the sampling list at the Aberdeen Proving Ground, Maryland wetland site. Analytes that required a constant, relatively high flowing sample stream to obtain accurate measurements, such as dissolved oxygen, commonly cannot be obtained for wetland porewater by current standard methods. Analysis of methane, ferrous iron, and sulfide, however, can be done on a total sample volume of 10 to 40 mL (depending on the concentrations). If one or more of these constituents are present in the sample in high concentrations, dissolved oxygen can be assumed to be negligible. To further limit the sample volume for the ESTCP wetland study and previous work at the Aberdeen

Proving Ground wetland site, VOCs were collected in 8 mL vials rather than the 40 mL vials commonly used. Another common problem encountered in sampling wetland porewater is that coloration of the water from natural organic carbon interfered with the colorimetric tests used to determine sulfide, ammonia, ferrous iron, requiring filtration (if not usually already filtered), dilution, or use of an alternative analytical method.

Microcosms can be used to assist in assessing biodegradation processes and rates in natural attenuation studies in wetlands but may require some additional considerations compared to other subsurface environments (Weidemeier et al. (1996). The typically high organic carbon content of wetland sediments may result in a large amount of sorption of the organic contaminants added to the microcosms. An estimate or measure of the sorption coefficients will assist in determining the amount of the contaminant to add to attain the desired dissolved or headspace concentrations in the microcosms. For microcosms constructed with wetland sediment from the Aberdeen Proving Ground site, about 1,100 ppb of TCE or 1,1,2,2-tetrachloroethene needed to be added to attain initial aqueous concentrations of 500 ppb (Lorah et al., 1997; 1999a). Killed controls are needed to assist in accounting the effect of sorption on VOC losses in the microcosms. In addition, the high biodegradation rates sometimes measured in organic-rich wetland sediments (Lorah et al., 1997, 1999a, in press) may require substantially shorter incubation times and sampling intervals than the 12 to 18 months suggested for microcosms with other subsurface sediments (Weidemeier et al., 1996).



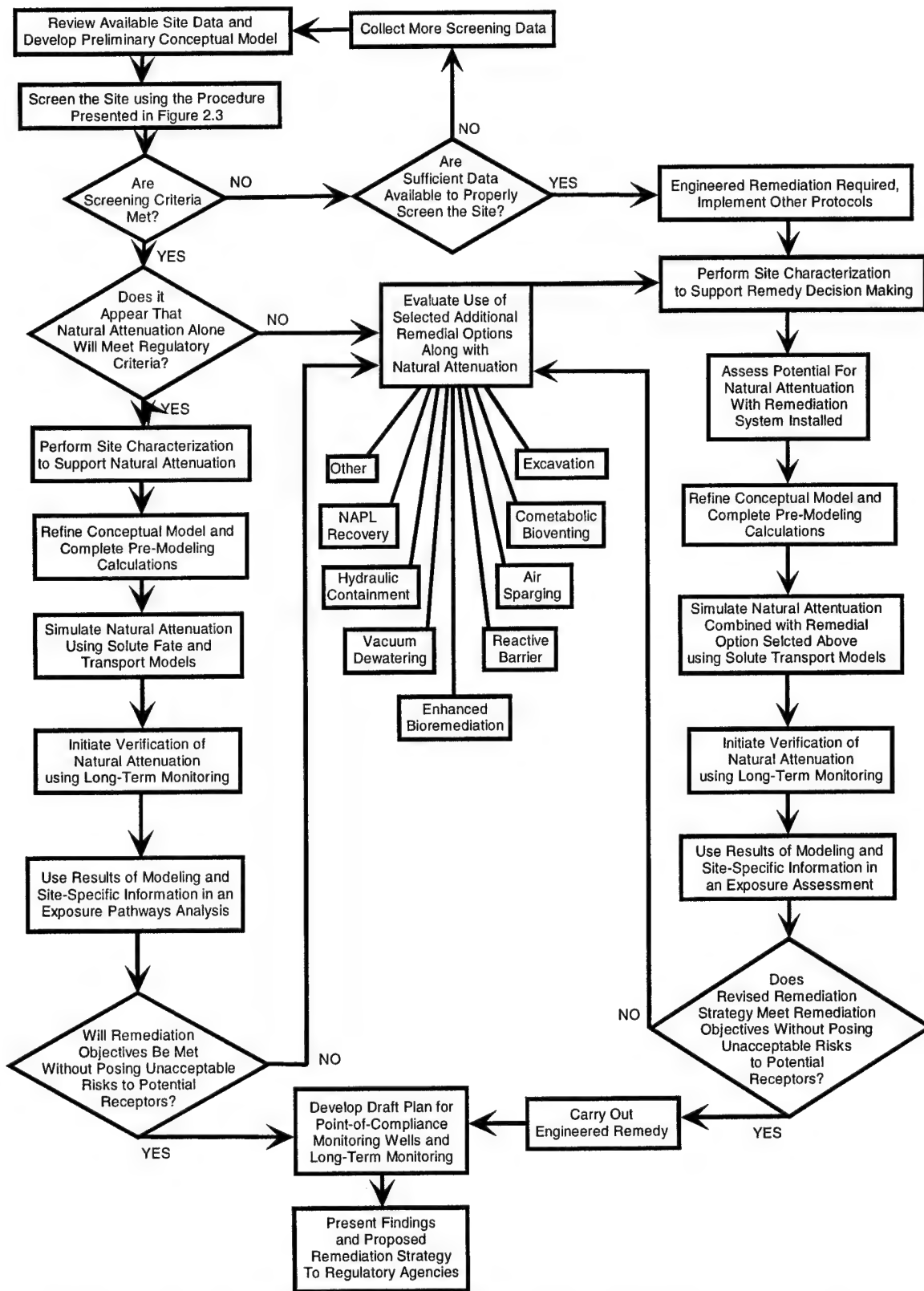
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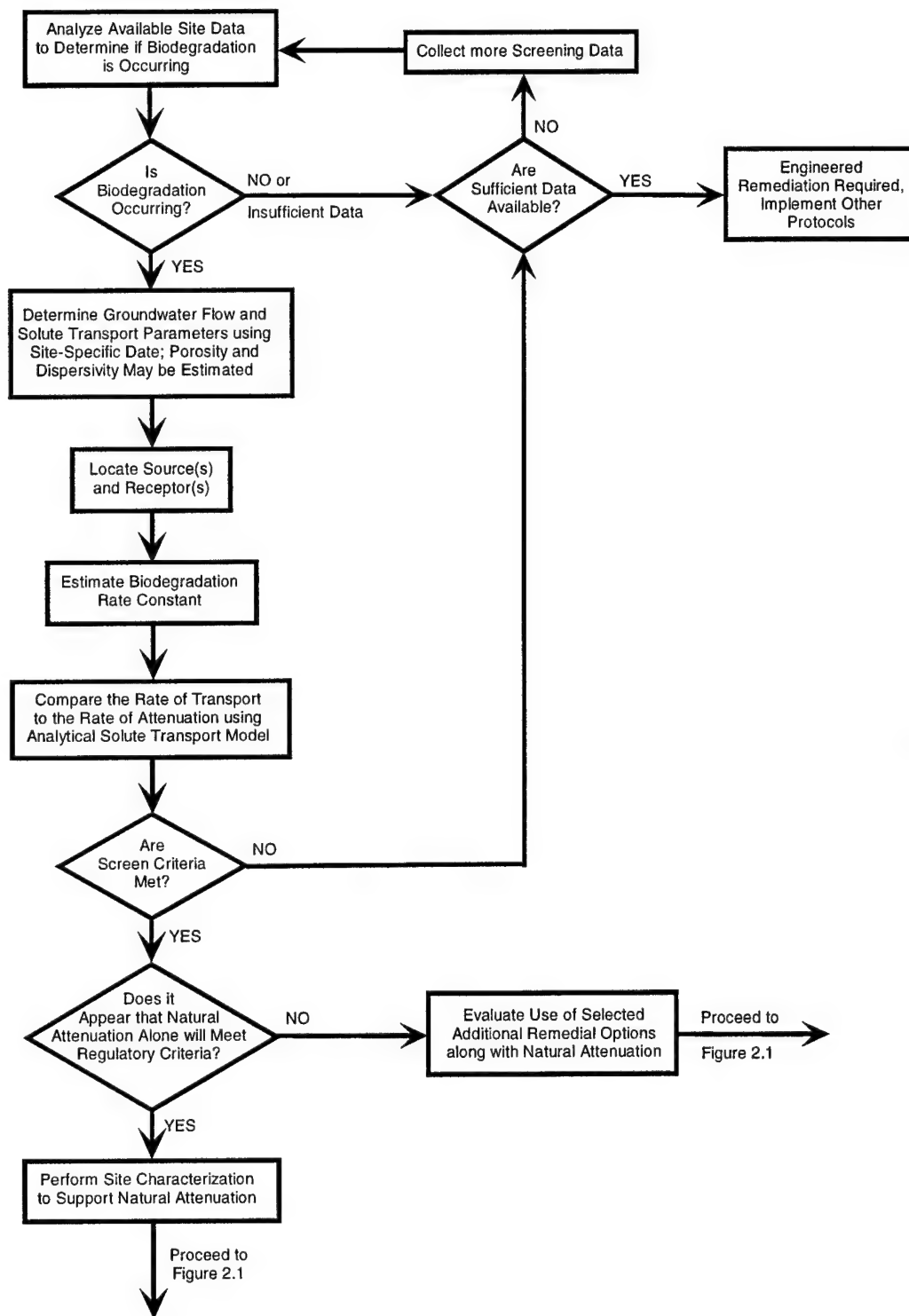
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**Figure 4.1.** Flow chart of the process of assessing natural attenuation of chlorinated solvents (from Wiedemeier et al., 1996, Figure 2.1).



**Figure 4.2.** Flow chart of the initial screening process in assessing natural attenuation of chlorinated solvents (from Wiedemeirer et al., 1996, Figure 2.3).

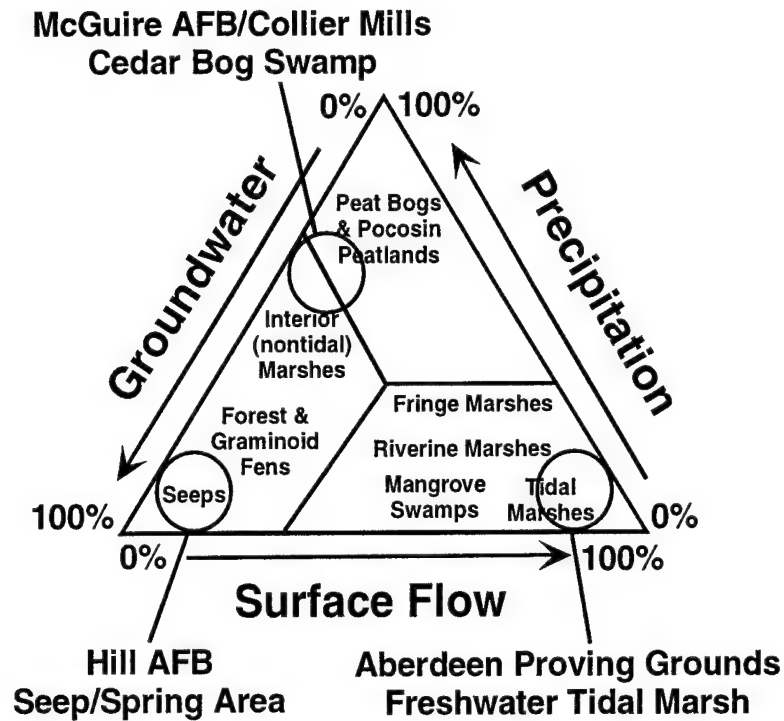


Figure 4.3. Classification of wetland study areas according to relative importance of water source (modified from Richardson, 1999, and Brinson, 1993).

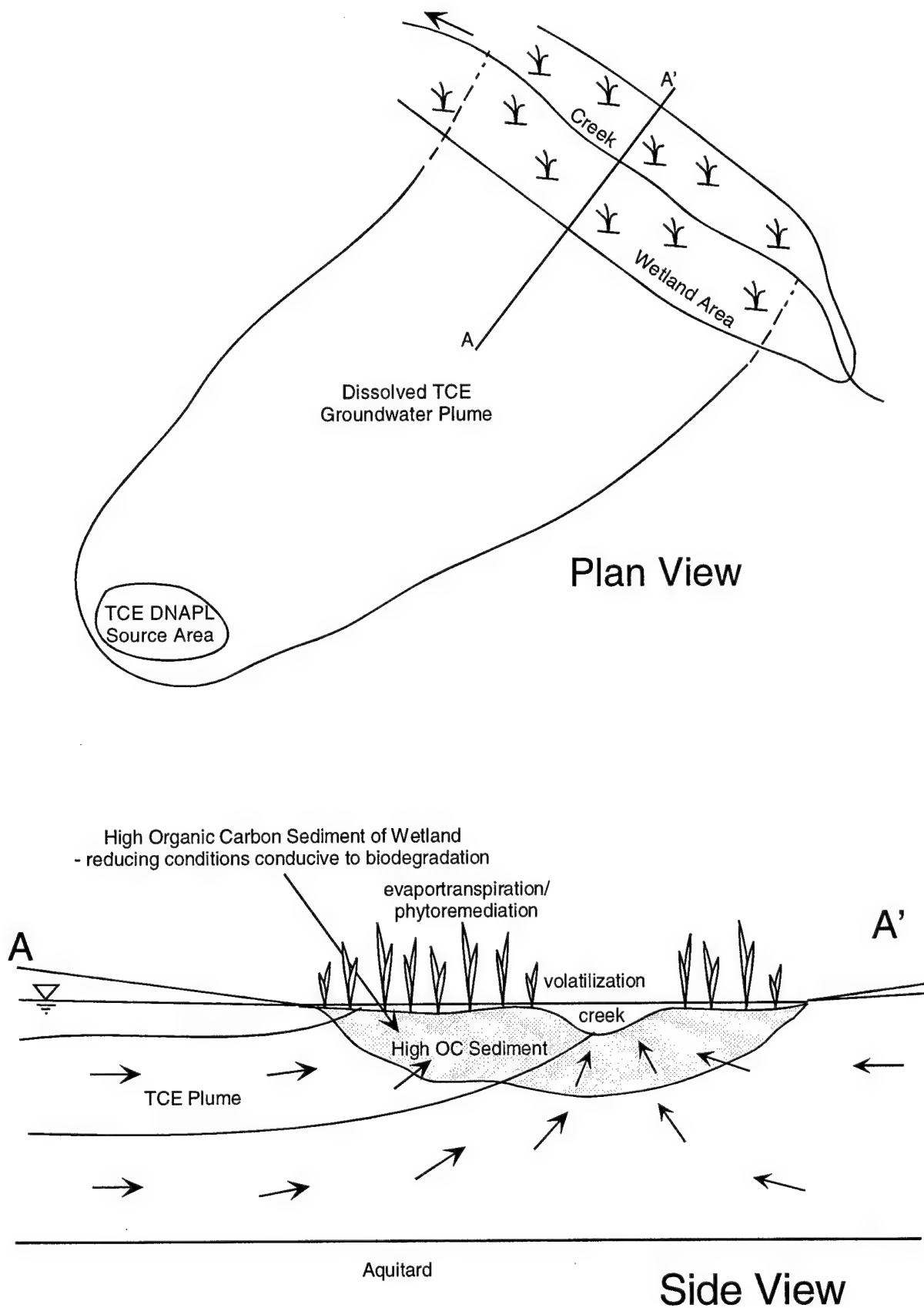


Figure 4.4. Example conceptual model for a chlorinated solvent plume discharging into a marsh or swamp wetland.



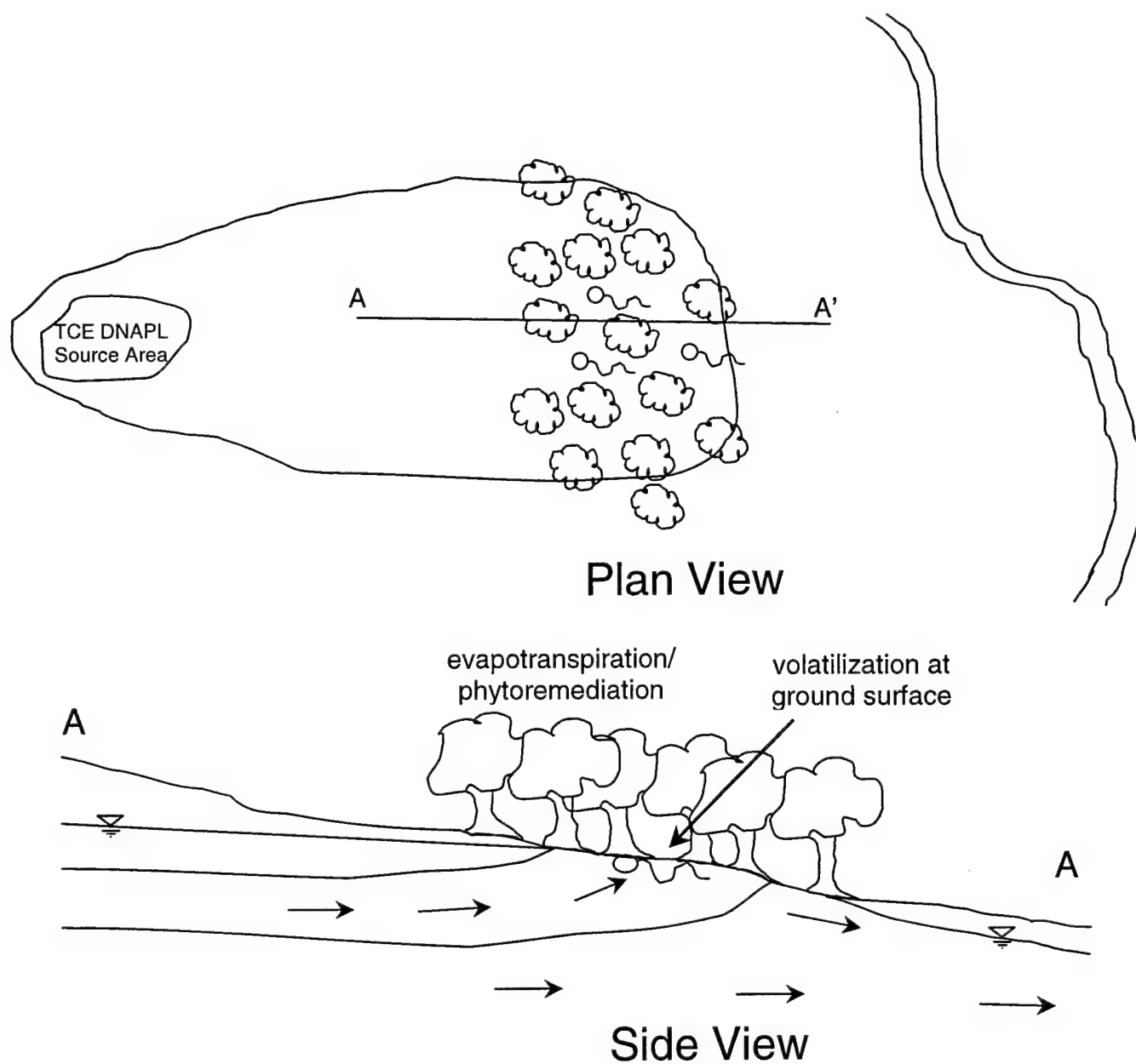


Figure 4.5. Example conceptual model for a chlorinated solvent plume discharging into a seep/spring wetland.

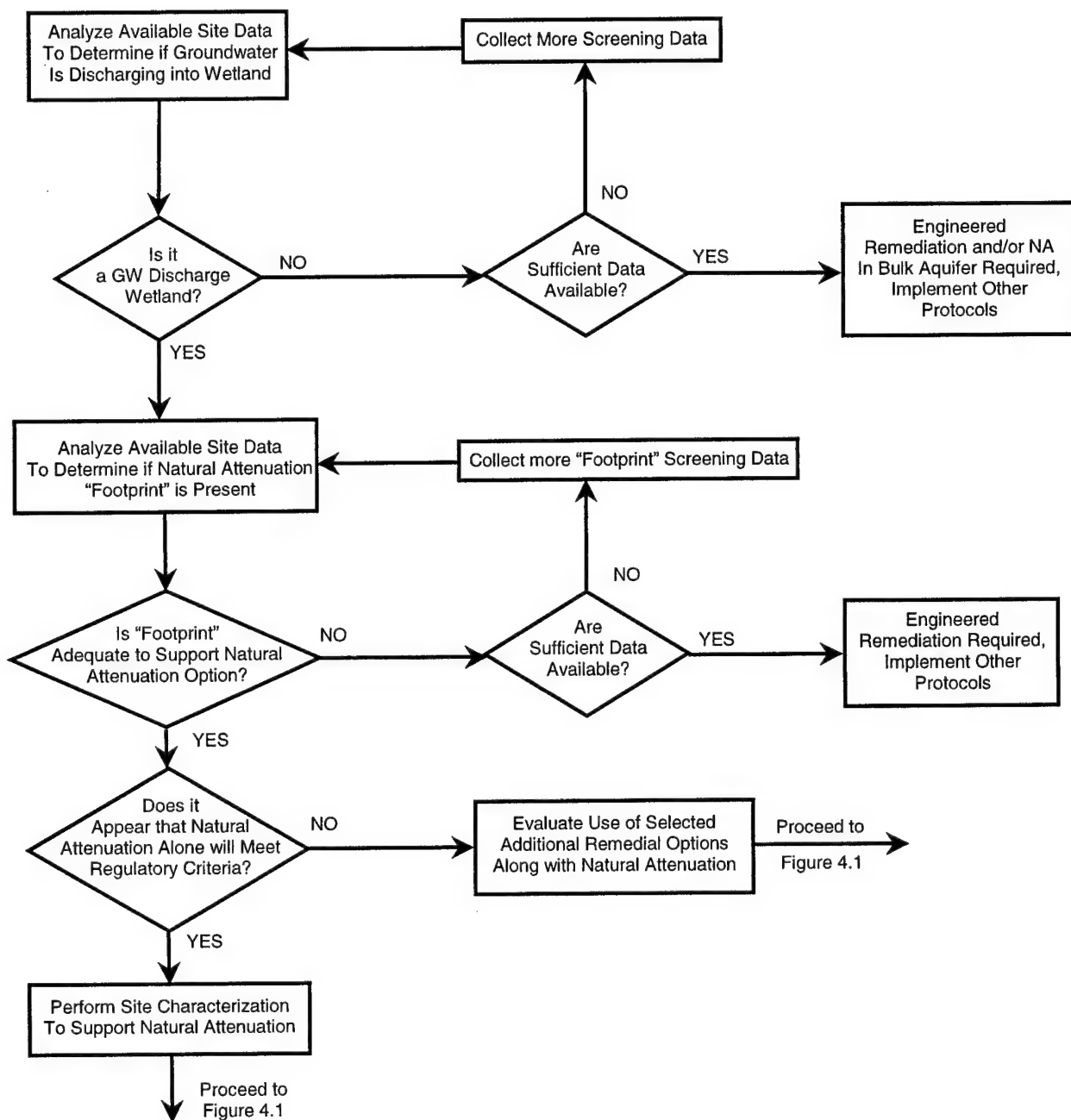


Figure 4.6. Initial screening process flowchart for evaluating natural attenuation of chlorinated solvents in wetlands.

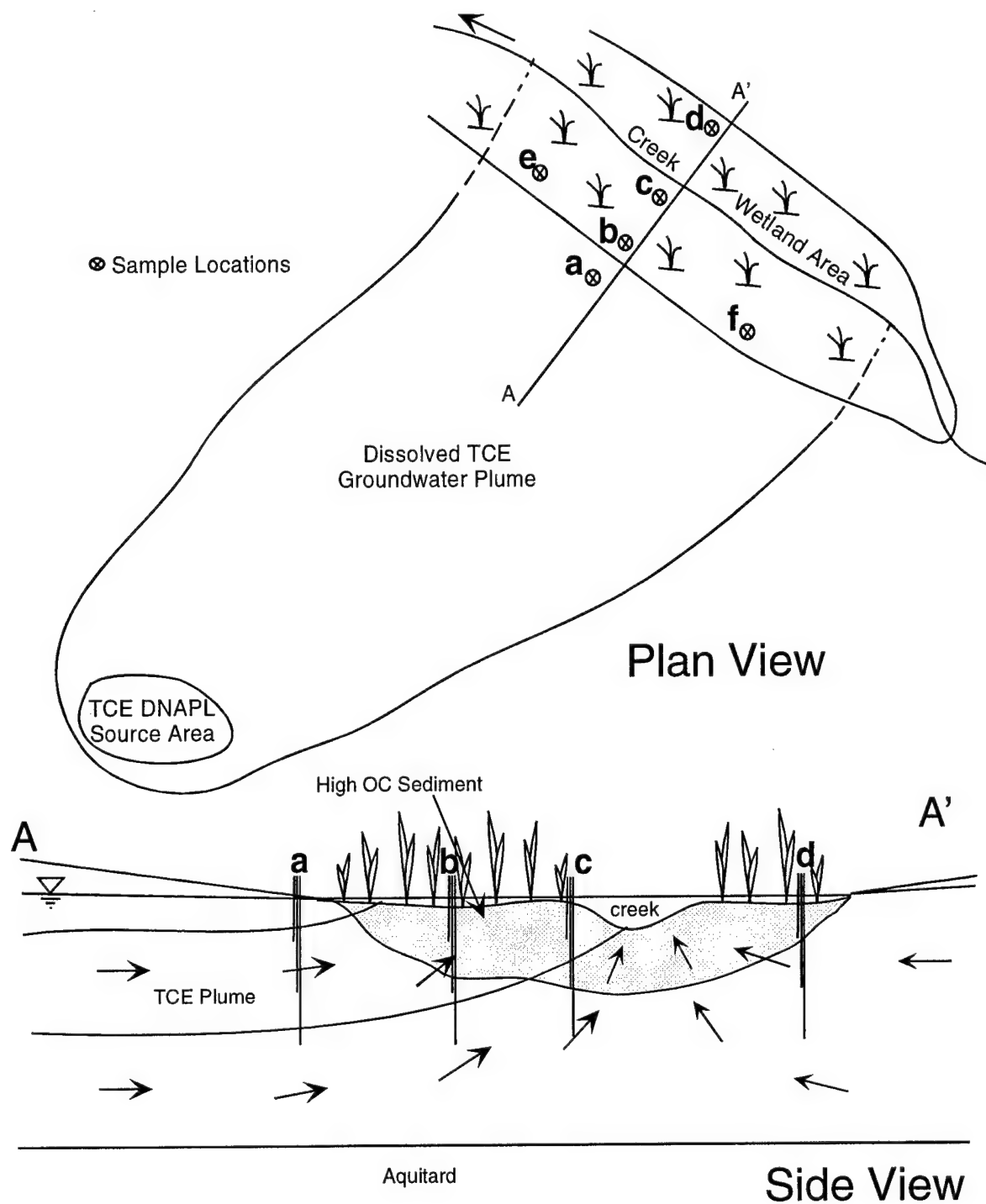


Figure 4.7. Schematic of additional data collection locations required for screening of natural attenuation of chlorinated solvents in wetlands (using the conceptual model shown in Figure 4.4).



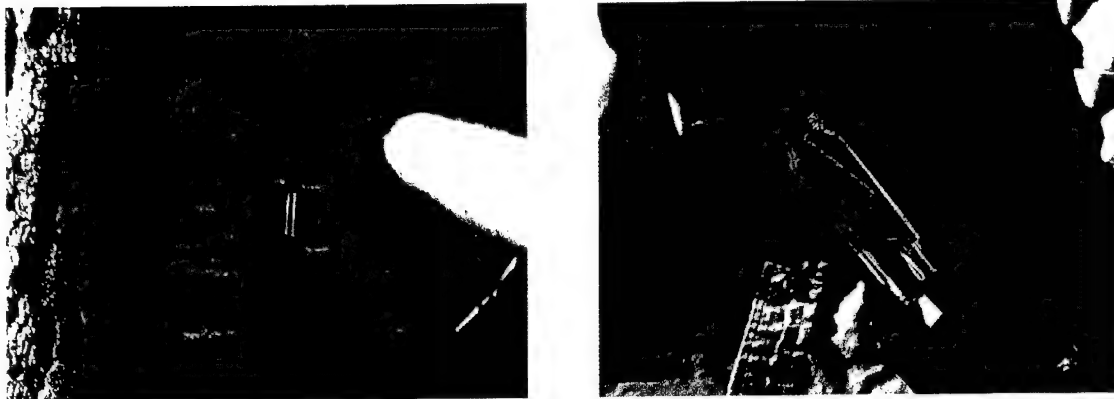
Figure 4.8. Split-spoon sampling using tripod and motorized hammer at the West Branch Canal Creek wetland site, Aberdeen Proving Grounds, Maryland.



**Figure 4.9.** Vibracore systems used at the West Branch Canal Creek wetland site at Aberdeen Proving Ground, Maryland. A: portable hydraulic unit with vibration only; B: portable hydraulic unit with vibration and hammer action; and C: Hoverprobe with attached hydraulic vibracore unit with vibration only.



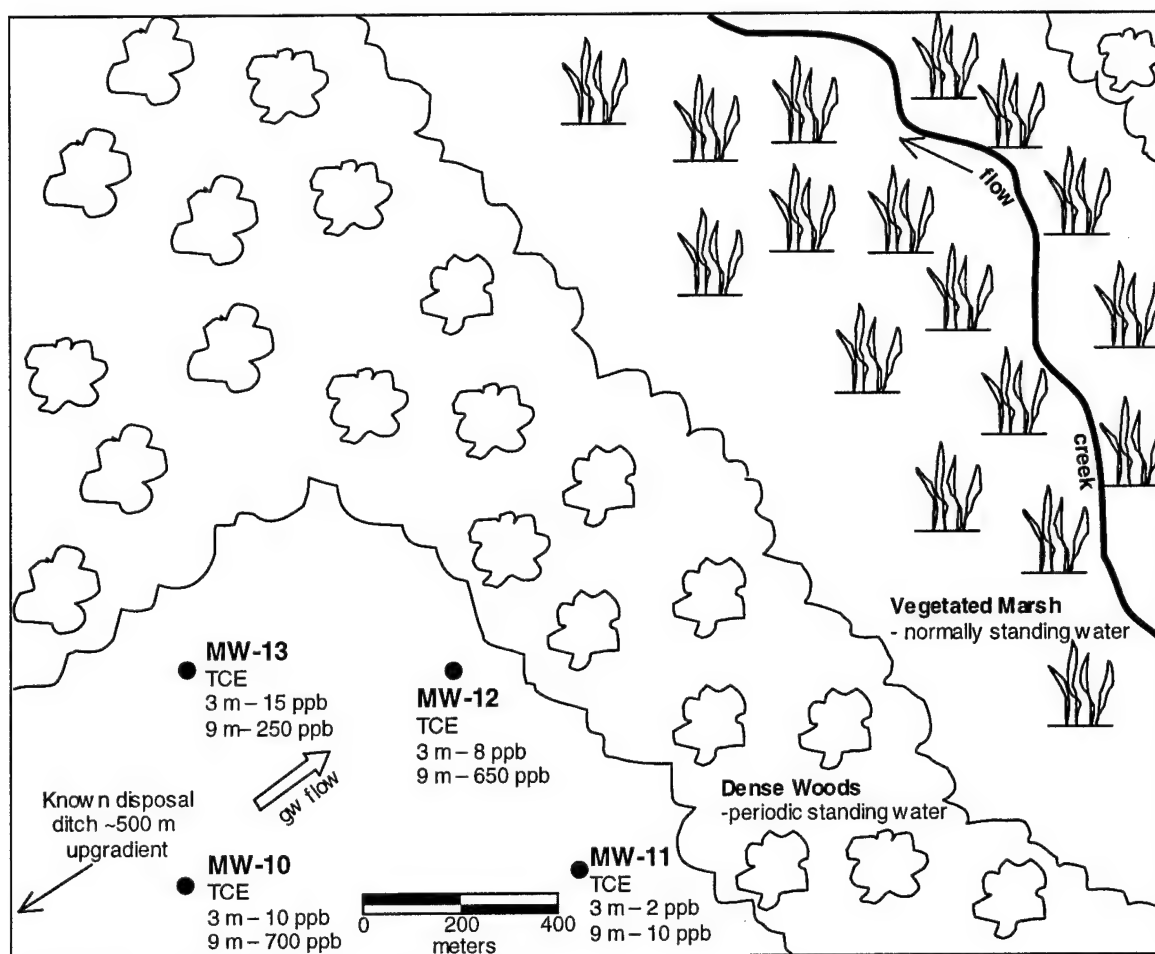
**Figure 4.10.** Direct push GeoProbe rig mounted onto a John Deere Gator. This drill rig was used at a McGuire AFB, NJ wetland site (Colliers Mills Wildlife Management Area) to obtain sediment cores and install drive point piezometers. The narrow width of the Gator can allow access to difficult-to-reach locations within some swamp-type wetlands.



**Figure 4.11.** Illustration of tree core sampling procedure for analysis of chlorinated volatile organic compounds: (a) tree coring using standard forestry coring device, and (b) addition of core to vial containing methanol for extraction.



**Figure 4.12.** Installation of narrow diameter drive-point piezometer using percussion hammer. Note the Teflon tubing inner sleeve extruding out of the hammer adapter. The Teflon tubing is connected by tubing barb to a stainless-steel drive-point tip with screens for ground-water inflow (Solinst Canada Ltd.).



#### EXPLANATION

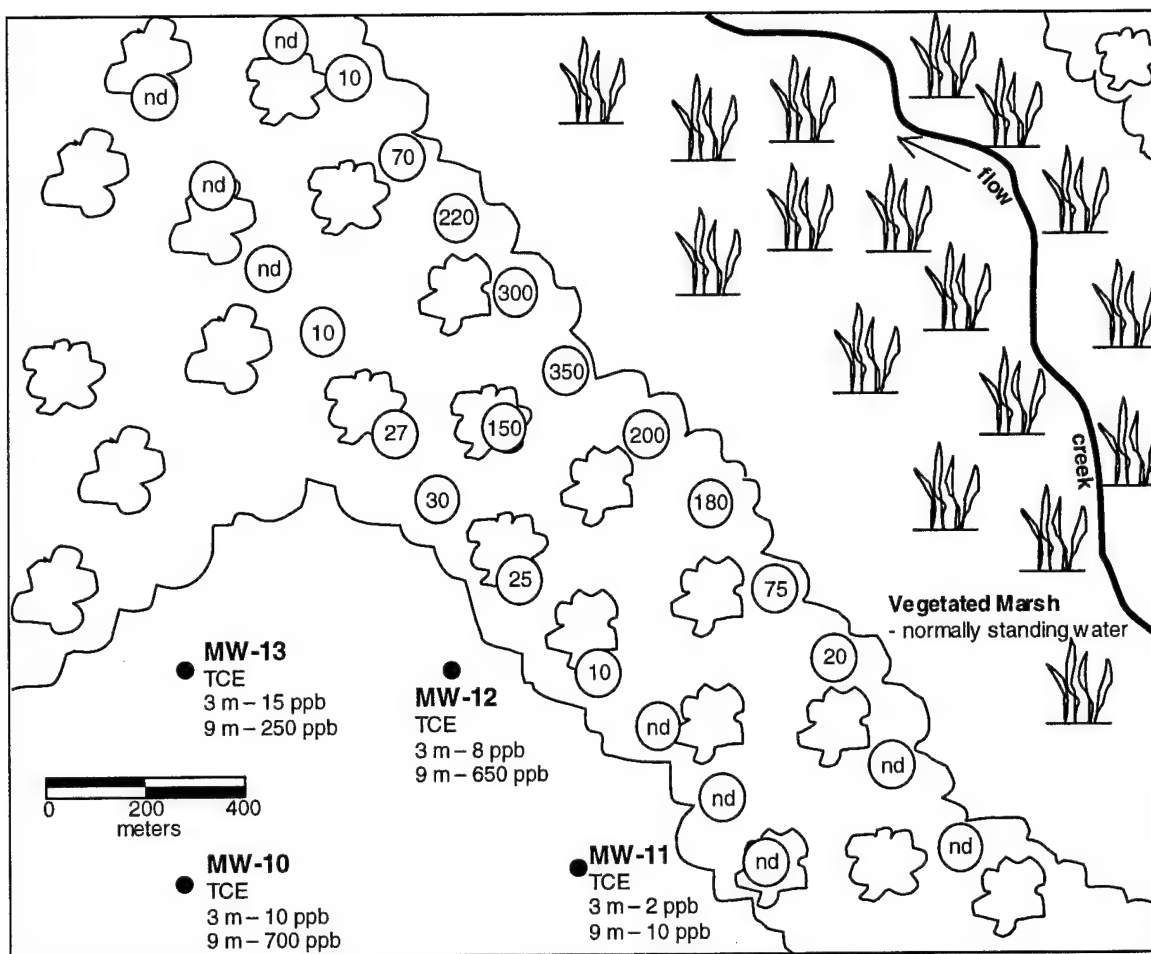
TCE, trichloroethene

gw flow, ground-water flow

3 m- 15 ppb screen depth in meters and TCE concentration in parts per billion

**Figure 4.13.** Schematic of a hypothetical site with a TCE ground-water contamination plume showing available site ground-water data closest to the wetland. Chlorinated anaerobic TCE degradation products (cis-12DCE or vinyl chloride) were either very low or non-detect.





#### EXPLANATION

TCE Trichloroethene

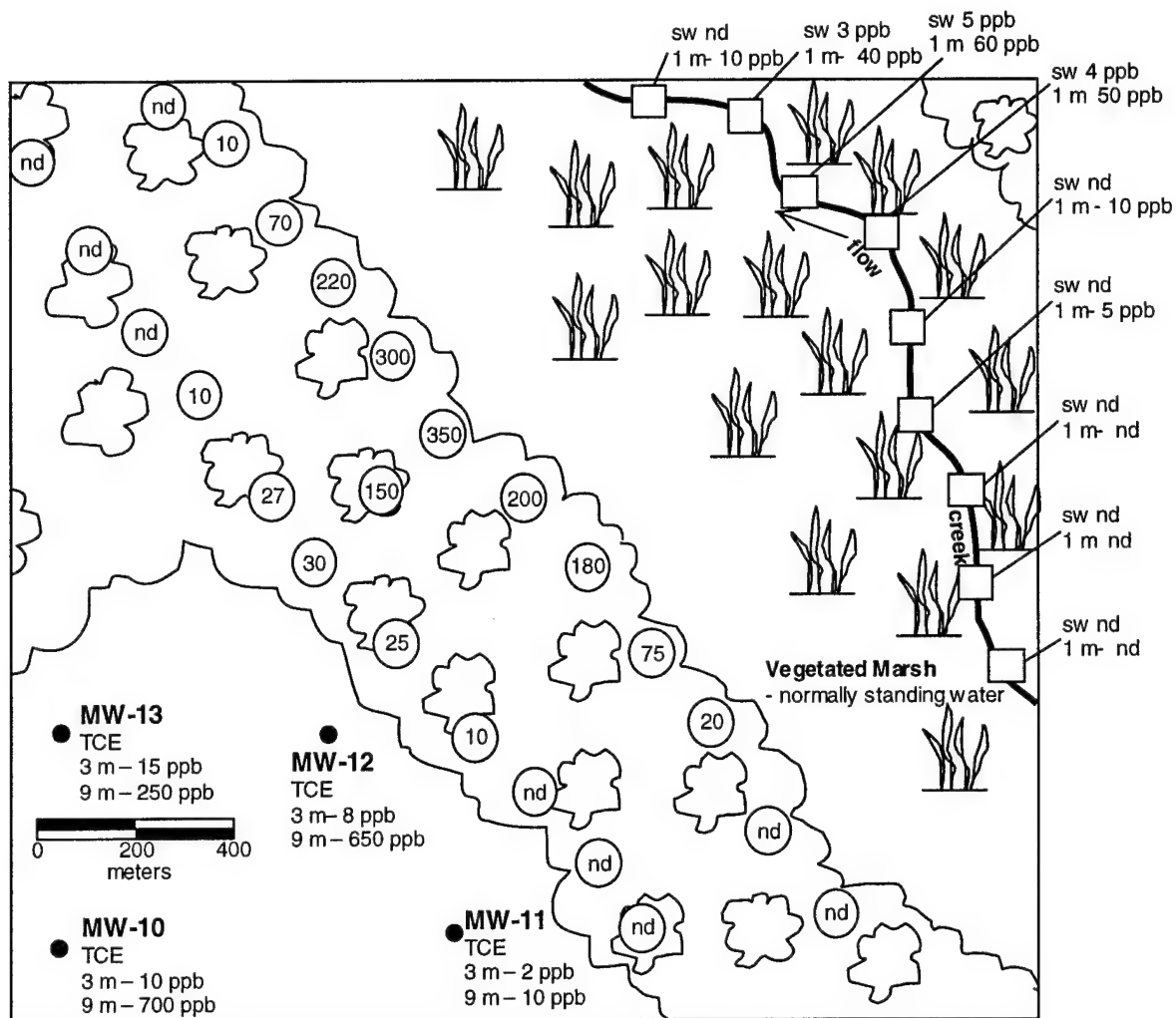
nd Not detectable

● MW-13 location of monitoring well and site number

3 m- 15 ppb screen depth in meters and TCE concentration in ground water in parts per billion

(25) TCE in tree core, in micrograms per kilogram

**Figure 4.14** Schematic of a hypothetical site with a TCE ground-water contamination plume showing tree core survey results of first phase of chlorinated solvent natural attenuation reconnaissance activity. Tree cores were taken at about 1.2 m above ground surface from pine trees of approximately the same size.



#### EXPLANATION

TCE Trichloroethene

nd Not detectable

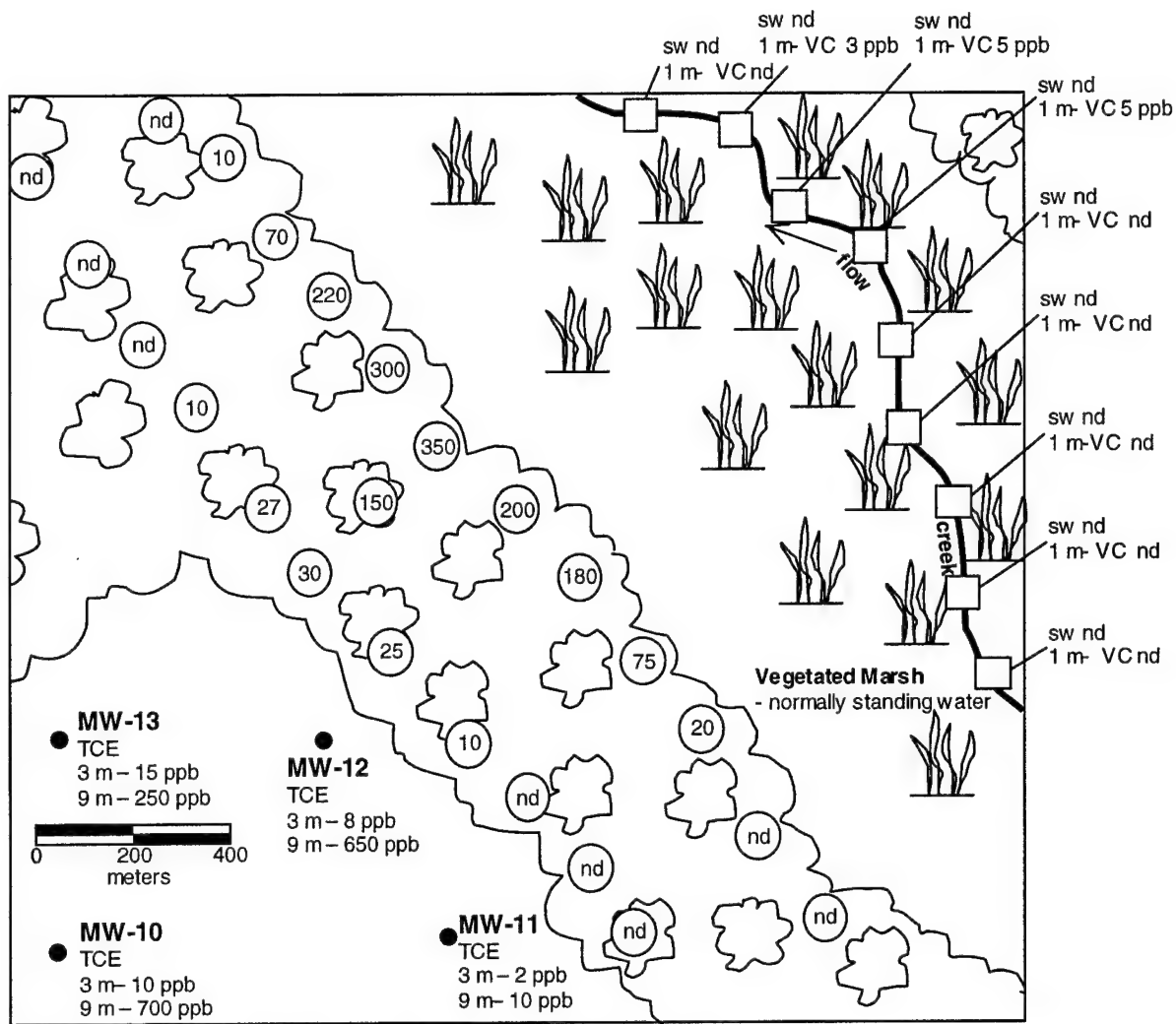
● **MW-13** location of monitoring well and site number

3 m- 15 ppb screen depth in meters and TCE concentration in ground water in parts per billion

□ Location of surface- water sampling site and streambed minipiezometer

(25) TCE concentration in tree core, in micrograms per kilogram

**Figure 4.15** Schematic of a hypothetical site with a TCE ground-water contamination plume showing TCE concentrations in surface water and sediment porewater (1 m depth using minipiezometers) from second phase of chlorinated solvent natural attenuation reconnaissance activity.



#### EXPLANATION

TCE Trichloroethene

nd Not detectable

● **MW-13** Location of monitoring well and site number

3 m - 15 ppb Screen depth in meters and TCE concentration in ground water in parts per billion

1 m- VC 5 ppb Screen depth in meters and vinyl chloride concentration in parts per billion

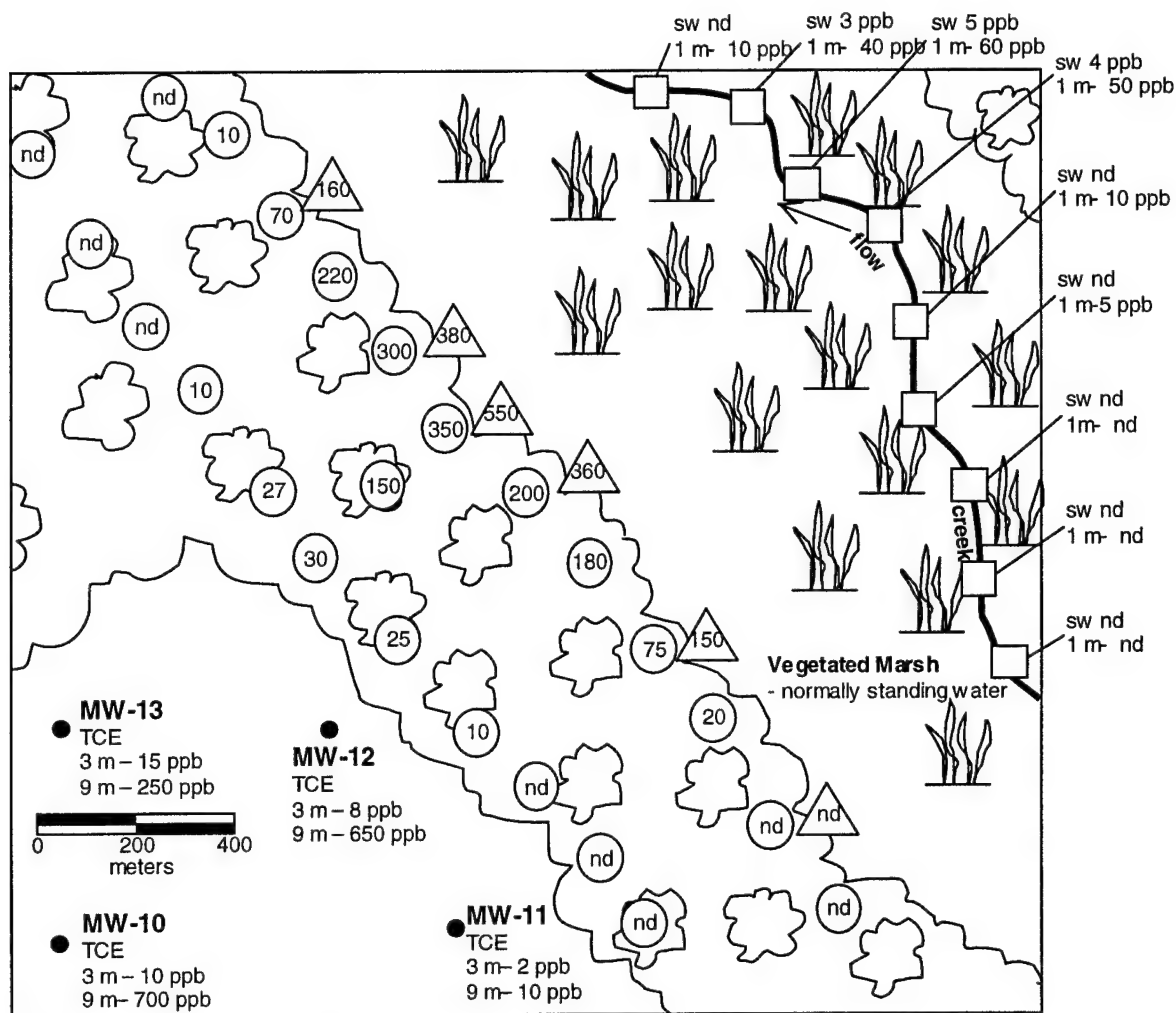


Location of surface- water sampling site and streambed minipiezometer



TCE in tree core in micrograms per kilogram

**Figure 4.16** Schematic of a hypothetical site with a TCE ground-water contamination plume showing VC concentrations in surface water and sediment porewater (1 m depth using minipiezometers) from second phase of chlorinated solvent natural attenuation reconnaissance activity.



#### EXPLANATION

TCE Trichloroethene

nd Not detectable

● MW-13 Location of monitoring well and site number

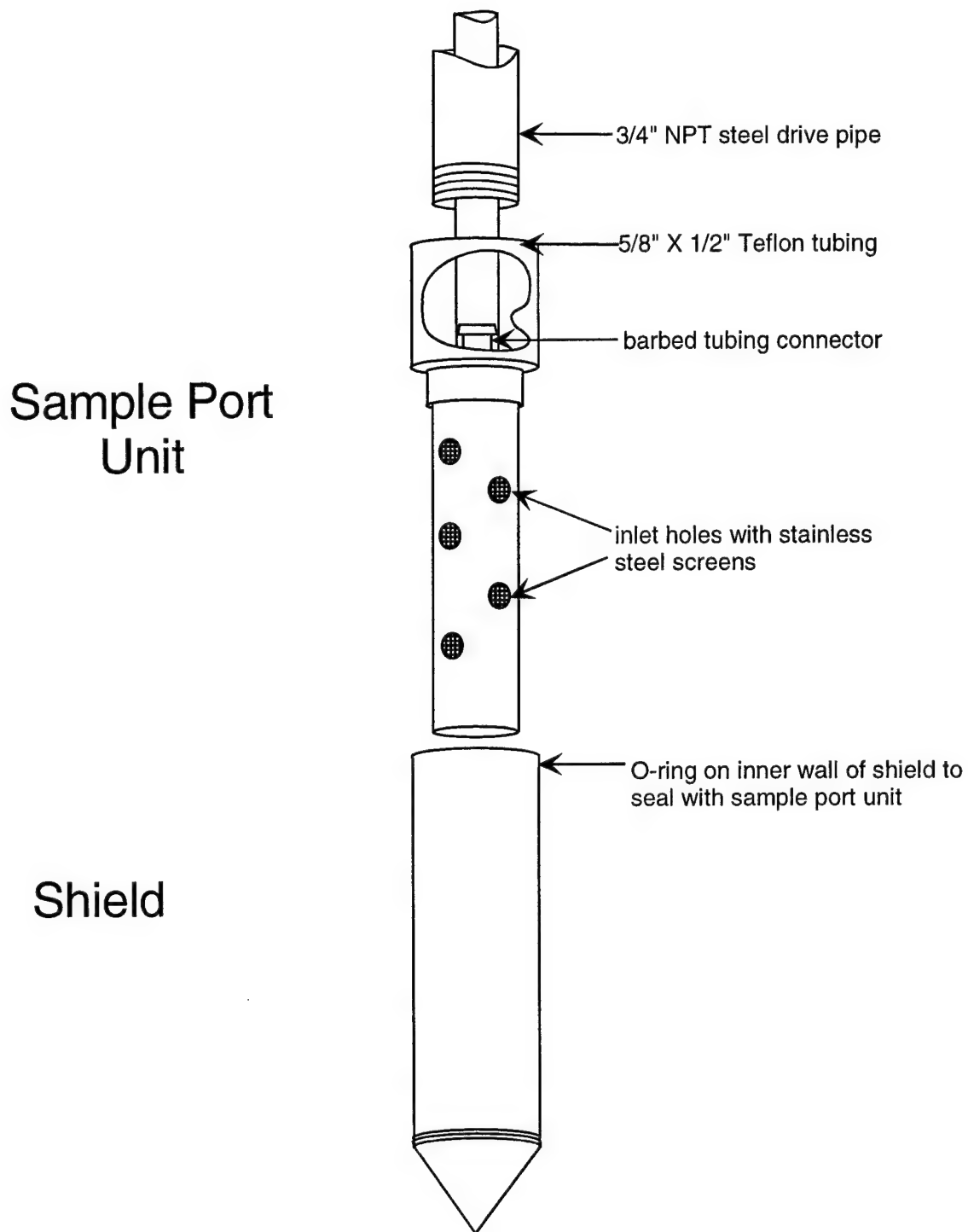
3 m- 15 ppb Screen depth in meters and TCE concentration in ground water in parts per billion

(25) TCE in tree core in micrograms per kilogram

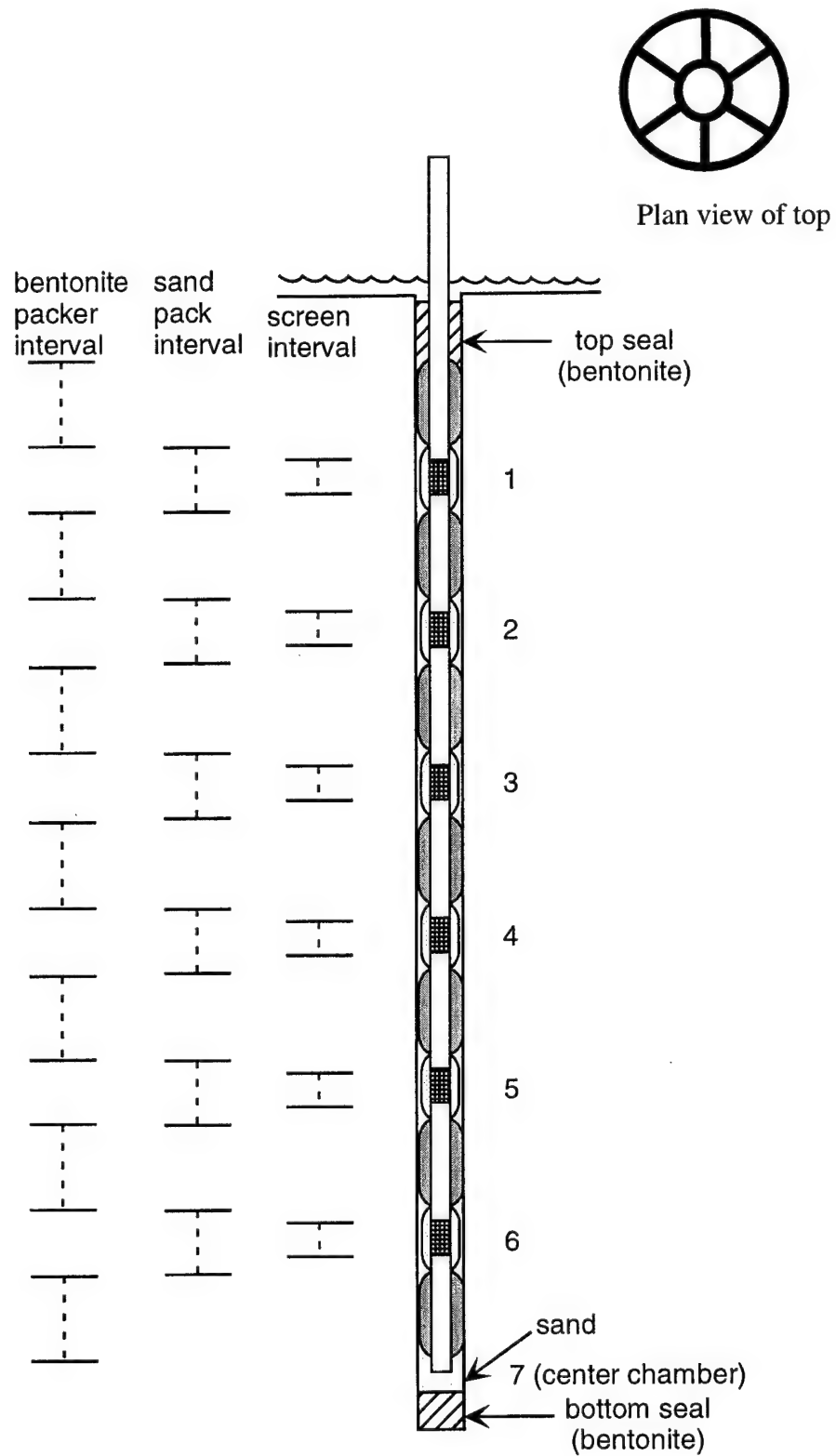
□ Location of surface- water sampling site and streambed minipiezometer

△ 100 Location of drive-point piezometer screened at 3.6 meters depth, and TCE concentration in parts per billion

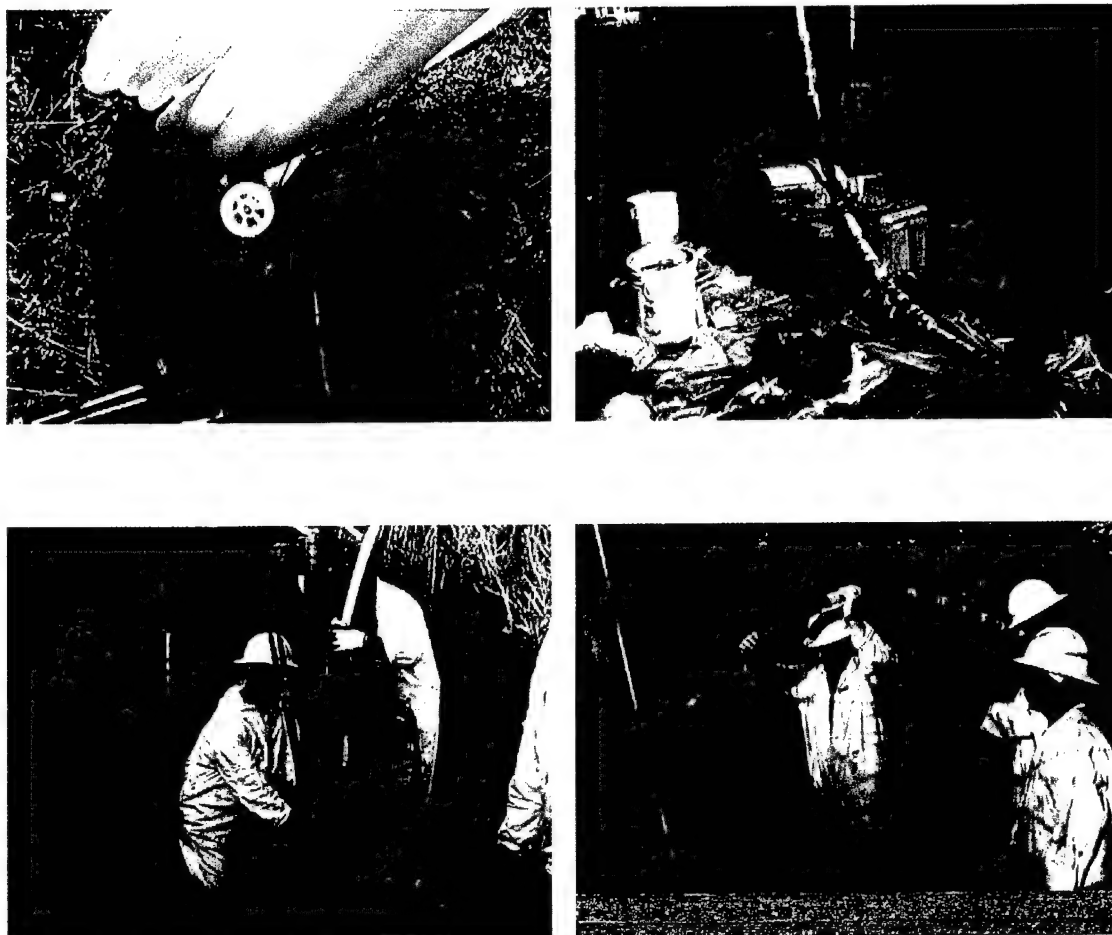
**Figure 4.17** Schematic of a hypothetical site with a TCE ground-water contamination plume showing concentrations of TCE in ground water (3.6 m depth using drive point piezometers) from third phase of chlorinated solvent natural attenuation reconnaissance activity.



**Figure 4.18.** Schematic of a Solinst Canada Ltd. Model 615S shielded drive-point piezometer.



**Figure 4.19.** Schematic of the Multi-level Monitoring System (Precision Sampling, Inc.) and emplacement within borehole.

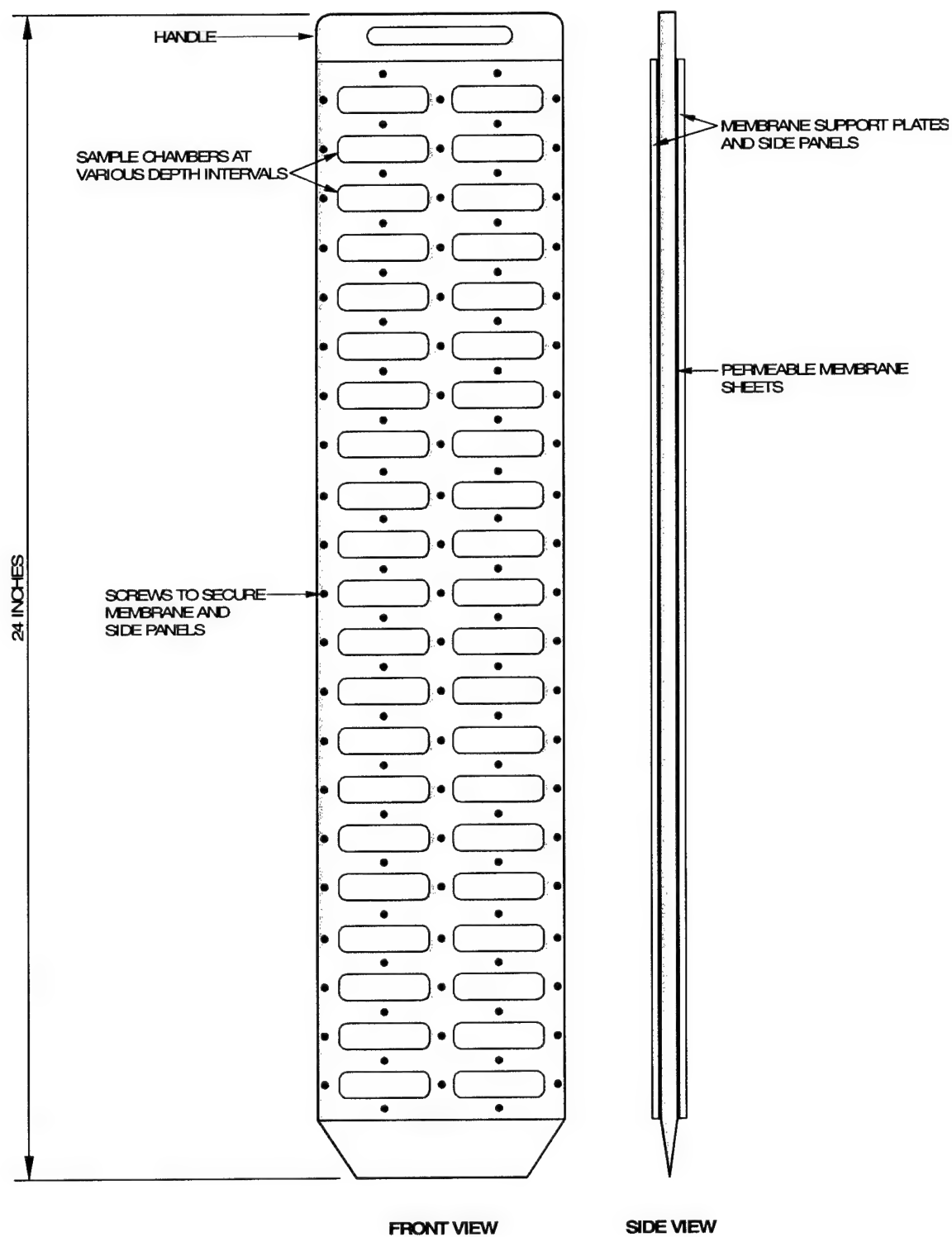


**Figure 4.20.** Preparation and installation of Multi-Level Monitoring System (MLMS; Precision Sampling, Inc.) at wetland study site: (A) coiled 7-chamber polyethylene tubing, (B) preparation of MLMS with sand packers and bentonite packers, (C) drilling of borehole with vibratory rig; and (D) insertion of MLMS down borehole casing. The borehole casing is immediately removed upon insertion of MLMS.

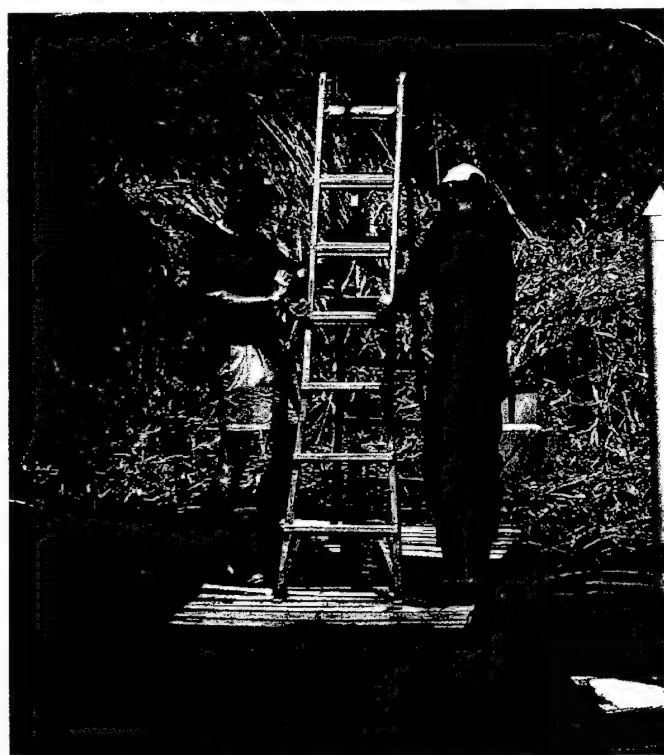
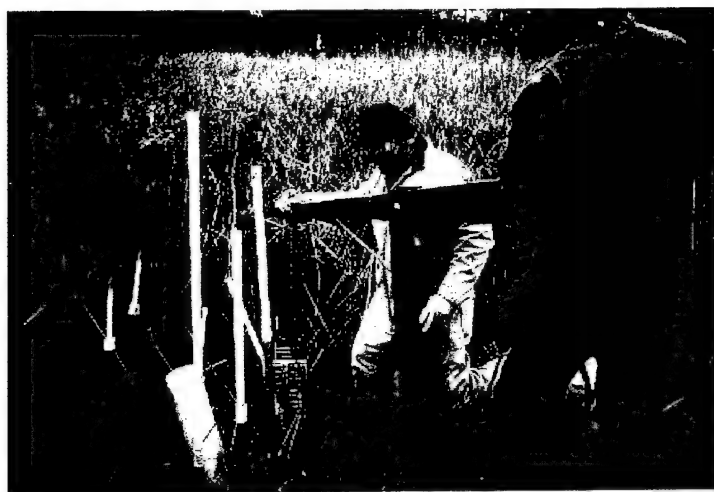


**Figure 4.21.** Photographs of (a) tubing and screen components of tubing sampler and (b) tubing sampler array at wetland field site. This extensive tubing sampler array was used for a detailed ground-water tracer study.

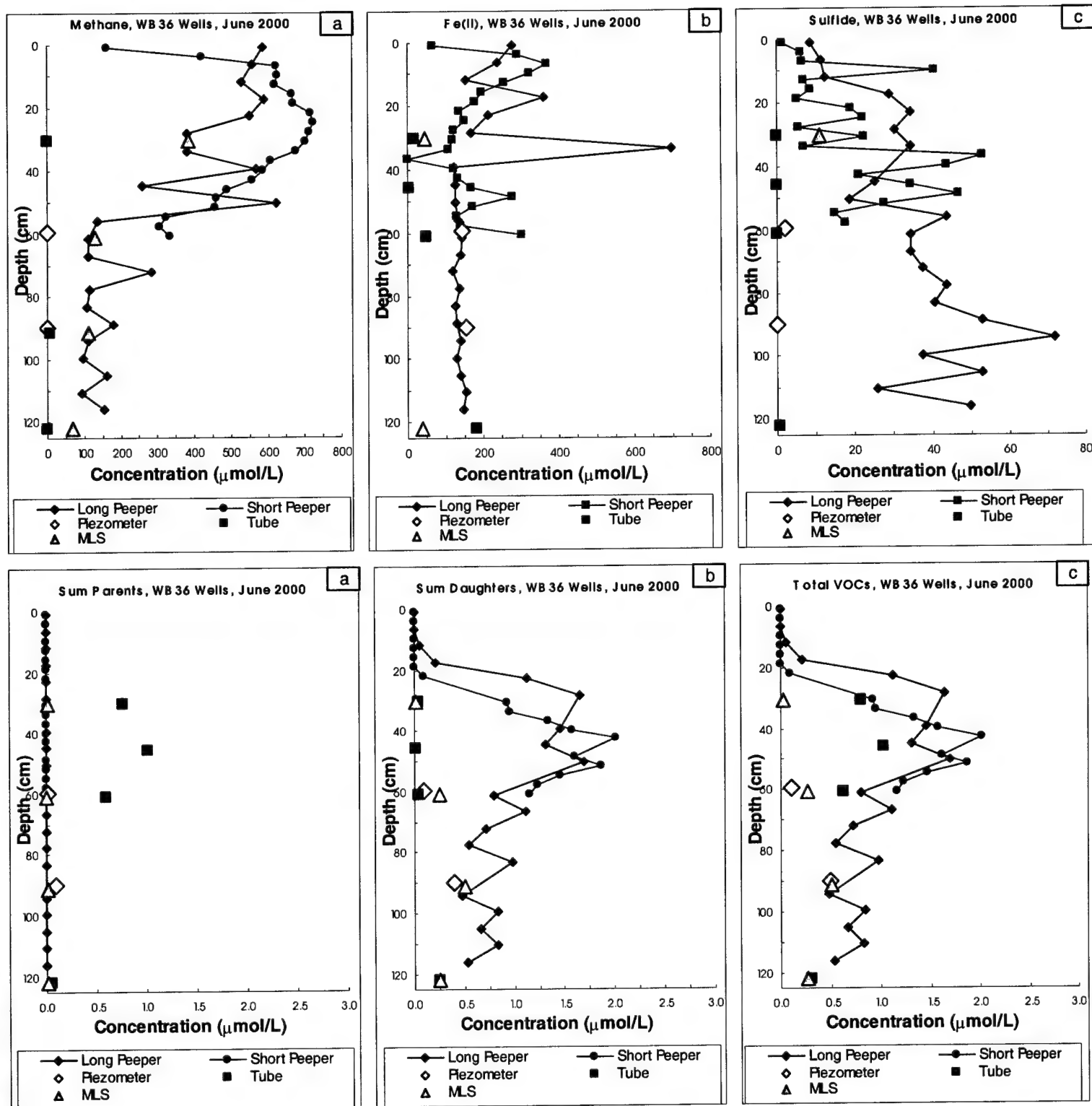




**Figure 4.22.** Schematic of a type of passive diffusion sampler that is commonly called a peeper.



**Figure 4.23.** Peeper passive diffusion sampler activities at Aberdeen Proving Ground, Maryland wetland field site: (A) pulling peeper out of wetland sediment using simple wooden lever system, and (B) withdrawing aqueous samples from peeper chambers for analysis of various biogeochemical parameters to assess natural attenuation of chlorinated solvents discharging into wetland; and at Norman, Oklahoma wetland site: (C) and (D) pulling peeper from streambed using a ladder and winch.



**Figure 4.24.** Concentrations of redox-sensitive constituents and of parent, daughter, and total VOCs in samples collected from peepers compared to other sampling devices installed at site WB36 at the West Branch Canal Creek wetland site, Aberdeen Proving Ground, Maryland.

## Appendix A. Points of Contact

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## **Appendix B. Data Archiving and Demonstration Plans**

Copies of both field and laboratory raw data sheets are filed as hard copies and electronically in two places: (1) all data related to the studies at Aberdeen Proving Ground, Maryland, and McGuire, Air Force Base, New Jersey are archived at U.S. Geological Survey, Baltimore, MD (Michelle M. Lorah); and (2) all data related to the Hill AFB study are archived at the Air Force Research Laboratory, Tyndall AFB, Florida (Christopher P. Antworth). There are 3 approved demonstration plans for this project. Copies of demonstration plans for the Aberdeen Proving Ground, Maryland, and McGuire, Air Force Base, New Jersey studies can be obtained at U.S. Geological Survey, Baltimore, MD (Michelle M. Lorah). Copies of demonstration plans for the Hill AFB study are archived at the Air Force Research Laboratory, Tyndall AFB, Florida (Christopher P. Antworth).

**Appendix C. Geochemical Data, Collier Mills Wildlife Management  
area, McGuire Air Force Base, New Jersey**

Table C-1. Collier Mills Wetland, New Jersey-- ESTCP Groundwater Sampling, Reconnaissance Phase

[--, not measured; Temp, water temperature; Cond, specific conductance; DO, dissolved oxygen; Fe<sup>2+</sup>, ferrous iron; Fe total, total dissolved iron; TCE, trichloroethene; cisDCE, cis-1,2-dichloroethene]

Site no.	Date	Temp (°C)	Cond (µS/cm)	pH	DO (mg/L)	Fe <sup>2+</sup> (mg/L)	Fe Total (mg/L)	Methane (ug/L)	Sulfide (mg/L)	TCE (ug/L)	Replicate Sample		
											cisDCE (ppb)	TCE (ug/L)	cisDCE (ug/L)
Piezometers													
CM1-1.5T	11/9/1999	--	--	--	--	--	--	--	--	0.6	<0.5	<0.5	<0.5
CM1-12	11/12/1999	--	--	--	--	--	--	--	--	<1	<1	--	--
CM2-1T	11/12/1999	--	--	--	--	--	--	--	--	2.0	<1	--	--
CM2-1.5T	11/12/1999	--	--	--	--	--	--	--	--	1.3	<1	1.4	<1
CM2-5	11/9/1999	11.4	44	--	0	3.93	3.95	<7	<0.03	25	1.4	--	--
CM2-12	11/12/1999	--	--	--	--	--	--	--	--	10	<1	--	--
CM3-1.5T	11/9/1999	--	--	--	--	--	--	--	--	1.6	<0.5	--	--
CM3-8	11/12/1999	--	--	--	--	--	--	--	--	110	4.9	100	4.7
CM3-8	12/9/1999	8.5	69	6.12	7.24	2.83	2.65	<8	0.01	--	--	--	--
CM3-12	11/9/1999	13.1	67	--	--	<0.05	0.05	<6	<0.01	220	7.1	--	--
CM3-12	12/8/1999	9.2	62	5.36	2.91	0.28	<0.05	<8	<0.01	130	6.3	--	--
CM4-1.5T	11/9/1999	--	--	--	--	--	--	--	--	<0.5	<0.5	--	--
CM4-12	11/12/1999	--	--	--	--	--	--	--	--	4.0	<1	2.8	<1
CM5-12	12/9/1999	--	--	--	--	--	--	--	--	<1	<1	--	--
CM6-12	12/9/1999	--	--	--	--	--	--	--	--	<1	<1	--	--
CM7-12	12/9/1999	--	--	--	--	--	--	--	--	<1	<1	--	--
CM8-5	12/9/1999	--	--	--	--	--	--	--	--	11	8.4	--	--
CM9-1T	11/12/1999	--	--	--	--	--	--	--	--	1.5	24	--	--
CM9-1T	12/9/1999	17.3	--	4.06	--	2.22	2.13	<8	0.01	--	--	--	--
CM9-3T	11/12/1999	--	--	--	--	--	--	--	--	58	130	--	--
CM9-3T	12/9/1999	12.4	--	5.33	--	1.99	1.82	30	0.03	--	--	--	--
CM9-5	11/12/1999	--	--	--	--	--	--	--	--	62	9.0	--	--
CM9-5	12/9/1999	9.5	--	5.94	--	2.24	2.07	<8	0.03	--	--	--	--
CM9-10.5	11/10/1999	--	--	--	--	--	--	--	--	32*	23*	--	--
CM9-21	11/10/1999	--	--	--	--	--	--	--	--	76	5.2	--	--
CM9-21	12/9/1999	--	65	5.69	--	--	2.37	<7	0.05	<1	9.6	--	--
CM10-0.5T	11/12/1999	--	--	--	--	--	--	--	--	<1	<1	--	--
CM10-0.5T	12/8/1999	--	--	--	--	--	--	<11	0.08	--	--	--	--
CM10-10	11/10/1999	--	--	--	--	--	--	--	--	13*	3.7*	--	--
CM10-12	12/8/1999	9.7	55	5.96	--	6.04	5.75	<8	<0.01	25	10	--	--
CM10-12	12/9/1999	--	--	--	--	4.33	4.57	--	--	--	--	--	--
CM10-20	11/11/1999	9.2	72	5.86	--	--	--	<8	--	130	5.5	--	--
CM10-20	12/9/1999	--	--	--	5.50	1.78	1.60	--	--	110	<1	--	--
CM11-1T	12/8/1999	--	--	--	--	--	--	<8	<0.01	5.7*	0.4*	--	--
CM11-20	11/11/1999	--	--	--	--	--	--	<8	--	29	4.9	28	5.2
CM11-20	12/8/1999	9.6	58	5.57	2.36	<0.05	<0.05	<7	0.03	41	5.8	--	--
CM12-1T	11/12/1999	--	--	--	--	--	--	--	--	5.4	<1	--	--
CM12-12	11/12/1999	--	--	--	--	--	--	--	--	32	5.1	32	4.5
CM12-12	12/8/1999	7.5	59	6.05	--	--	--	<8	--	36	4.5	51	<1
CM12-12	12/9/1999	11.4	58	5.36	--	0.41	0.39	--	0.01	--	--	--	--
CM12-23	11/11/1999	--	--	--	--	--	--	--	--	170	3.6	170	3.6
CM12-23	11/12/1999	--	--	--	--	--	--	--	--	240	4.6	240	3.7
CM12-23	12/8/1999	--	80	5.94	2.81	1.50	1.39	<8	<0.01	260	5.7	--	--
CM13-1T	12/8/1999	--	75	4.85	--	0.25	0.24	<8	0.05	130	6.3	--	--
CM13-2T	11/12/1999	--	--	--	--	--	--	--	--	150*	16*	--	--
CM13-2T	12/7/1999	--	--	--	--	--	--	<8	--	--	--	--	--
CM13-2T	12/8/1999	--	--	--	--	<0.05	<0.05	--	--	--	--	--	--
CM13-2T	12/9/1999	--	--	--	--	--	--	<7	0.01	--	--	--	--
CM13-12	11/11/1999	--	--	--	--	--	--	--	--	480	9.0	--	--

CM13-12	11/12/1999	--	--	--	--	--	--	--	--	190	8.9	186	9.4
CM13-12	12/7/1999	8.4	--	--	3.32	--	--	<7	--	240	15	280	16
CM13-21	12/7/1999	--	--	--	--	--	--	--	--	210	6.3	--	--
CM13-21	11/11/1999	--	--	--	--	--	--	--	--	270	5.8	--	--
CM13-21	11/12/1999	--	--	--	--	--	--	--	--	185	3.0	220	6.1
CM13-21	12/7/1999	8.4	62	--	5.43	<0.05	<.050	<8	0.03	220	3.2	--	--
CM14-2T	11/12/1999	--	--	--	--	--	--	--	--	<1	<1	<1	<1
CM14-2T	12/7/1999	9.7	33	--	--	3.88	3.55	<9	0.64	<1	<1	<1	<1
CM14-5	11/12/1999	--	--	--	--	--	--	--	--	11	<1	2.9	<1
CM14-5	12/7/1999	9.2	69	--	0.89	5.35	3.84	<8	0.36	<1	<1	--	--
CM15-12	11/11/1999	--	--	--	--	--	--	<8	--	1.5	<1	1.1	<1
CM16-10	11/12/1999	--	--	--	--	--	--	--	--	19	<1	--	--
CM16-10	12/9/1999	--	--	--	--	--	--	--	--	5.5	<1	--	--
CM16-28	11/12/1999	--	--	--	--	--	--	--	--	380	17	360	15
CM16-28	12/9/1999	--	--	--	--	--	--	--	--	490	21	--	--
CM17-12	12/9/1999	--	--	--	--	--	--	--	--	2.6	<1	--	--
CM17-23	12/9/1999	--	--	--	--	--	--	--	--	430	18	420	18
ST1-1	11/12/1999	--	--	--	--	--	--	--	--	21	48	15	37
ST1-1	12/8/1999	--	55	5.23	--	<0.05	0.06	<8	0.03	180	5.5	--	--
ST1-3	11/11/1999	--	--	--	--	--	--	--	--	120	2.3	--	--
ST2-1	11/12/1999	--	--	--	--	--	--	--	--	180	29	--	--
ST2-1	12/7/1999	--	--	--	--	0.11	0.15	12	--	<1	13	--	--
ST2-3	11/11/1999	--	--	--	--	--	--	<8	0.09	170	3.9	190	4.8
ST3-1	11/12/1999	--	--	--	--	--	--	--	--	160	4.4	--	--
ST3-1	12/7/1999	--	--	--	--	<0.05	0.09	<9	--	110	7.0	170	10
ST3-4	11/11/1999	--	--	--	--	--	--	--	--	350	4.0	170	3.7
ST4-1	12/9/1999	10.4	61	4.59	--	0.19	0.18	<8	<0.01	<1	<1	--	--
ST4-3	12/9/1999	11.1	58	5.80	--	<0.05	3.15	<8	0.01	2.5	<1	--	--
SWBT-1	11/12/1999	--	--	--	--	--	--	--	--	1.1	7.7	--	--
SWBT-3	11/12/1999	--	--	--	--	--	--	--	--	1.0	2.5	--	--
<b>Surface water</b>													
SWB	11/11/1999	--	--	--	--	--	--	--	--	<1.0	<1.0	--	--
S-8	11/10/1999	--	--	--	--	--	--	--	--	67.9	2.46	--	--
S-9	11/10/1999	--	--	--	--	--	--	--	--	31.0	3.60	--	--
S-10	11/10/1999	--	--	--	--	--	--	--	--	14.0	1.70	--	--
S-11	11/10/1999	--	--	--	--	--	--	--	--	0.80	<0.50	--	--
S-12	11/10/1999	--	--	--	--	--	--	--	--	0.77	<0.50	--	--
S-13	11/11/1999	--	--	--	--	--	--	--	--	32.2	1.47	--	--
S-14	11/11/1999	--	--	--	--	--	--	--	--	35.6	1.45	--	--
S-15	11/11/1999	--	--	--	--	--	--	--	--	36.2	1.46	--	--
S-16	11/11/1999	--	--	--	--	--	--	--	--	29.7	1.33	--	--
S-17	11/11/1999	--	--	--	--	--	--	--	--	25.1	1.08	--	--
S-18	11/11/1999	--	--	--	--	--	--	--	--	<1.0	1.04	--	--
S-19	11/11/1999	--	--	--	--	--	--	--	--	<1.0	<1.0	--	--



Table C5. Volatile organic compounds and redox-sensitive constituents in peeper samples, ESTCP Sampling, September 2000, BOMARC Missile Facility, McGuire AFB, NJ/Collier Mills WMA Wetland Site

[µg/L, micrograms per liter; --, no data; E, estimated value; Fe2+, ferrous iron analyzed colorimetrically]

Sample date	Collection date	Sample depth (cm)	<i>trans</i> -1,2- <i>cis</i> -1,2-			Benzene (µg/L)	Toluene (µg/L)	Fe2+ (mg/L)	Sulfide (µg/L)	Methane (µg/L)
			Trichloro-ethene (µg/L)	Dichloro-ethene (µg/L)	Dichloro-ethene (µg/L)					
PCM3-1	9/19/2000	0.75	<.5	<.5	<.5	<.5	<.5	--	--	<59
PCM3-2	9/19/2000	3.75	<.5	<.5	<.5	<.5	<.5	27.2	<20	1,410
PCM3-3	9/19/2000	6.75	<.5	<.5	<.5	1.3	13.6	23.4	--	3,820
PCM3-5	9/19/2000	12.75	1.4	<.5	.7	<.5	29.0	28.9	100	8,810
PCM3-6	9/19/2000	15.75	2.3 E	<.5	1.6 E	<.5	--	27.7	170	8,740
PCM3-6	9/19/2000	15.75	1.8	<.5	1.3	<.5	16.6	--	--	--
PCM3-7	9/19/2000	18.75	2.8	<.5	4.6	.5	28.3	28.4	230	8,480
PCM3-8	9/19/2000	21.75	3.8 E	<.5	8.4 E	1.1 E	--	24.9	230	7,530
PCM3-8	9/19/2000	21.75	4.8	.5	7.1	<.5	9.2	--	--	--
PCM3-9	9/19/2000	24.75	5.9	.7	7.8	<.5	18.2	26.0	280	6,420
PCM3-10	9/19/2000	27.75	6.0	<.5	3.7	<.5	6.3	23.8	200	5,640
PCM3-11	9/19/2000	30.75	4.8	<.5	3.1	<.5	10.5	26.4	310	--
PCM3-12	9/19/2000	33.75	3.3	<.5	1.7	<.5	4.2	22.4	380	4,640
PCM3-13	9/19/2000	36.75	4.4	<.5	1.8	<.5	6.7	0.49	--	--
PCM3-14	9/19/2000	39.75	4.2	<.5	2.8	<.5	6.6	15.5	--	--
PCM9-1	9/19/2000	0.75	.8	<.5	<.5	1.1	36.5	5.63	180	8,040
PCM9-2	9/19/2000	3.75	1.8	<.5	<.5	1.0	31.1	5.16	370	6,700
PCM9-4	9/19/2000	9.75	4.5	<.5	.7	<.5	48.6	1.99	380	6,220
PCM9-5	9/19/2000	12.75	2.4	<.5	.8	<.5	<.5	5.00	240	5,870
PCM9-6	9/19/2000	15.75	4.8	<.5	1.2	<.5	<.5	5.63	160	4,710
PCM9-7	9/19/2000	18.75	8.3	<.5	1.0	<.5	1.9	7.29	--	3,320
PCM9-8	9/19/2000	21.75	11.6	<.5	2.3	<.5	12.2	7.61	190	3,520
PCM9-9	9/19/2000	24.75	20.8	<.5	3.2	<.5	14.9	7.21	620	3,410
PCM9-10	9/19/2000	27.75	22.0	<.5	1.5	<.5	.8	6.18	640	2,820
PCM9-11	9/19/2000	30.75	23.6	<.5	3.4	<.5	1.0	6.03	590	2,430
PCM9-12	9/19/2000	33.75	30.1	<.5	2.0	<.5	4.1	5.08	450	2,220
PCM9-13	9/19/2000	36.75	35.1	<.5	1.9	.5	4.4	5.63	460	2,110
PCM9-14	9/19/2000	39.75	45.8	<.5	2.1	.8	3.3	8.87	540	1,970
PCM9-15	9/19/2000	42.75	35.8	<.5	3.6	.6	4.0	10.1	420	1,870
PCM9-16	9/19/2000	45.75	42.3	<.5	2.1	.9	2.3	11.5	450	2,230
PCM9-17	9/19/2000	48.75	39.4	<.5	4.0	.5	3.8	8.64	180	--
PCM9-18	9/19/2000	51.75	42.9 E	<.5	2.7 E	.9 E	.5	8.87	300	1,500
PCM9-18	9/19/2000	51.75	46.3	<.5	1.9	.7	1.3	--	--	--
PCM9-19	9/19/2000	54.75	33.5	<.5	3.0	.8	.8	7.37	210	1,420
PCM9-20	9/19/2000	57.75	36.6 E	<.5	.9 E	<.5	1.0	8.24	570	1,760
PCM9-20	9/19/2000	57.75	49.8	<.5	1.7	.9	3.0	--	--	--
PCM9-21	9/19/2000	60.75	48.8	<.5	.8	1.8	4.2	12.1	500	1,710
PCM13-1	9/19/2000	0.75	3.5 E	<.5	8.5 E	<.5	<.5	0.88	67	99
PCM13-1	9/19/2000	0.75	1.8	<.5	6.2	1.3	<.5	--	--	--
PCM13-2	9/19/2000	3.75	5.6 E	<.5	11.5 E	1.3 E	.8	0.73	1,020	218
PCM13-2DUP	9/19/2000	3.75	2.7	<.5	9.8	<.5	<.5	--	--	--
PCM13-3	9/19/2000	6.75	2.5	<.5	29.4	1.3	3.0	0.57	950	581
PCM13-3DUP	9/19/2000	6.75	.8	<.5	35.1	1.7	8.3	--	--	--
PCM13-4	9/19/2000	9.75	2.0	<.5	61.7	1.0	3.4	0.65	720	1,780
PCM13-5	9/19/2000	12.75	1.6	.5	83.1	1.8	.9	0.65	420	1,360
PCM13-6	9/19/2000	15.75	2.3	1.0	195	.8	<.5	0.41	380	1,240
PCM13-7	9/19/2000	18.75	.6	.9	191	.5	<.5	0.57	300	837
PCM13-8	9/19/2000	21.75	3.8	<.5	82.0	.9	<.5	0.81	220	713
PCM13-8DUP	9/19/2000	21.75	1.0	.8	141	4.6	<.5	--	--	--
PCM13-9	9/19/2000	24.75	4.7	<.5	67.4	.8	<.5	0.33	220	555
PCM13-10	9/19/2000	27.75	2.3	.8	138	.6	<.5	0.73	210	989
PCM13-11	9/19/2000	30.75	2.9	.8	109	.8	<.5	0.96	200	331
PCM13-12	9/19/2000	33.75	2.0	.7	95.9	4.9	<.5	0.65	370	322
PCM13-13	9/19/2000	36.75	3.8	.5	67.0	.8	<.5	0.65	330	238
PCM13-14	9/19/2000	39.75	7.0	<.5	18.9	<.5	<.5	0.65	520	144
PCM13-15	9/19/2000	42.75	5.2	<.5	11.6	<.5	<.5	0.41	10	102
PST4-1	9/19/2000	0.975	.9	<.5	121	1.2	<.5	1.12	1,100	1,620
PST4-2	9/19/2000	6.461	.9	.5	115	<.5	<.5	1.68	1,100	2,480
PST4-3	9/19/2000	11.947	55.3	<.5	10.3	<.5	<.5	0.73	730	2,710
PST4-4	9/19/2000	17.433	1.2	<.5	95.4	<.5	<.5	0.41	720	2,200
PST4-5	9/19/2000	22.919	2.7	<.5	88.6	<.5	.5	<0.2	910	1,280
PST4-6	9/19/2000	28.405	8.5	<.5	74.8	<.5	<.5	<0.2	670	601
PST4-7	9/19/2000	33.891	20.2	<.5	47.0	<.5	<.5	<0.2	800	496
PST4-8	9/19/2000	39.377	18.4 E	<.5	79.8 E	<.5	<.5	<0.2	450	671
PST4-9	9/19/2000	44.863	1.0	.6	106	<.5	<.5	<0.2	460	102
PST4-10	9/19/2000	50.349	69.2 E	<.5	3.3 E	<.5	<.5	<0.2	280	<41
PST4-10	9/19/2000	50.349	62.8	<.5	4.0	<.5	<.5	--	--	--
PST4-12	9/19/2000	61.321	60.1	<.5	1.6	<.5	<.5	<0.2	--	--

Table C6. Water-quality data, ESTCP Sampling, March 2001, BOMARC Missile Facility, McGuire AFB, NJ/Coiller Mills WMA Wetland Site

[D in well name, duplicate; TCE, trichloroethene; c12DCE, cis-1,2-dichloroethene; t12DCE, trans-1,2-dichloroethene; VC, vinyl chloride; Fe2+, ferrous iron; CH4, methane; DOC, dissolved organic carbon; N.D., not detected; <, less than]

Well	Date Collected	TCE (ug/L)	c12DCE (ug/L)	t12DCE (ug/L)	VC (ug/L)	Benzene (ug/L)	p-isopropyl-toluene (ug/L)	Toluene (ug/L)	FeTot (ppm)	Fe2+ (ppm)	CH4 (ug/L)	Sulfide (ppm)	Sulfate, Dissolved (mg/L)	Chloride, Dissolved (mg/L)	DOC (mg/L)	Nitrate (mg/L)	Ammonia (mg/L)	Dissolved Oxygen (mg/L)	pH	Specific Cond. (uS/cm)
WELLS																				
CM1-1.5T	4/2/2001	ND	ND	ND	ND	ND	ND	0.41	ND	1.21	1804	0.08	3.41	2.40	ND	ND	ND	ND	ND	ND
CM1-12	4/2/2001	<5	ND	ND	ND	ND	ND	ND	1.21	1.21	<34.7	0.08	12.45	3.52	3	ND	ND	ND	4.44	ND
CM2-1.5	4/5/2001	1.97	ND	ND	<5	ND	ND	ND	0.69	0.64	<43.1	0.04	13.74	3.29	3	ND	ND	ND	ND	ND
CM2-2	4/5/2001	0.94	<5	ND	<5	ND	ND	ND	5.28	4.88	ND	0.04	8.28	3.37	4	<2.5	1	ND	5.15	45
CM2-5	4/3/2001	1.45	ND	ND	ND	ND	ND	ND	8.54	8.54	48	0.04	ND	ND	3	<2.5	0.1	ND	ND	ND
CM2-12	3/30/2001	39.25	3.25	ND	<5	ND	ND	1.91	4.92	4.88	570	0.15	7.48	2.99	8	<2.5	0.1	5.3	6.36	63
CM3-0.7	3/31/2001	5.43	2.08	ND	<5	ND	ND	16.77	7.59	7.51	8474	ND	1.53	4.36	95	<2.5	4	ND	4.14	76
CM3-8	3/31/2001	221.27	16.25	<5	<5	ND	ND	<5	2.57	2.53	721	<0.1	15.32	2.55	9	<2.5	0.6	7.6	5.23	88
CM3-12	3/28/2001	203.1	6.34	<5	ND	ND	ND	ND	0.10	0.07	<28.9	0.05	29.96	2.99	8	<2.5	0.1	2.4	5.2	11
CM3-16	3/31/2001	14.13	4.11	ND	ND	ND	ND	<5	5.40	5.42	<38.0	<0.1	32.38	2.89	39	<2.5	1	ND	5.35	141
CM3-31	4/3/2001	146.97	9.59	<5	<5	ND	ND	ND	3.64	3.64	<42.5	0.01	19.76	2.11	2	<2.5	<0.1	ND	5.71	108
CM3-33	3/31/2001	267.98	6.42	<5	<5	ND	ND	0.77	0.14	0.12	<33.8	0.01	22.26	2.40	7	<2.5	<0.1	3.6	4.27	80
CM4-12	3/30/2001	<5	ND	ND	<5	ND	<5	0.94	10.4238	10.748	1446	ND	4.42	6.40	ND	<2.5	0.1	8.2	5.43	46
CM4-17	3/30/2001	<5	ND	ND	<5	ND	ND	ND	1.98	1.92	<35.6	0.01	16.80	6.48	6	<2.5	0.1	ND	5.72	95
CM4-34	3/30/2001	57.87	8.42	ND	ND	ND	ND	ND	11.59	11.31	<43.3	<0.1	35.95	2.18	ND	<2.5	0.6	1.0	5.5	146
CM5-1.6T	4/2/2001	ND	<5	ND	ND	ND	ND	<5	ND	ND	82	ND	14.43	3.63	13	<2.5	0.1	ND	ND	ND
CM5-12	4/2/2001	ND	ND	ND	<5	ND	ND	<5	2.25	2.25	202	0.04	9.86	3.63	19	<2.5	0.1	1.7	5.69	42
CM6-12	4/2/2001	ND	ND	ND	<5	ND	ND	<5	3.03	3.02	113	0.03	9.88	3.08	6	<2.5	0.1	8.2	5.43	46
CM6-12D	4/3/2001	<5	<5	ND	<5	ND	ND	ND	1.70	1.69	55	<0.1	10.95	2.96	3	<2.5	0.1	7.1	ND	ND
CM7-12	4/2/2001	ND	ND	ND	ND	ND	ND	ND	1.60	1.60	73	0.01	10.80	2.42	3	<2.5	0.1	5.4	4.84	41
CM8-5	4/2/2001	ND	2.38	ND	<5	ND	ND	0.47	ND	ND	256	ND	20.58	2.73	4	<2.5	0.1	ND	6.28	84
CM8-5D	4/3/2001	ND	1.9	ND	<5	ND	ND	ND	2.52	2.51	201	0.05	19.68	2.38	2	<2.5	0.1	ND	ND	ND
CM9-1T	3/29/2001	2.98	140.37	1.98	0.91	ND	ND	ND	0.79	0.76	62	0.03	9.07	3.51	8	ND	ND	ND	4.92	ND
CM9-3T	3/29/2001	60.66	172.31	0.99	1.13	ND	ND	<5	3.61	3.63	741	0.12	17.78	4.08	10	ND	ND	2.6	5.02	106
CM9-5	3/28/2001	72.96	8.71	<5	ND	ND	ND	ND	0.94	0.95	<36.4	<0.1	13.47	3.10	6	<2.5	<0.1	6.4	5.71	62
CM9-10.5	3/29/2001	7.00	<5	ND	ND	ND	ND	<5	9.44	9.36	40	<0.1	17.33	5.22	9	<2.5	0.3	4.7	5.51	88
CM9-21	3/31/2001	426.41	9.96	<5	<5	ND	ND	<5	2.73	2.51	<36.2	<0.1	17.95	2.41	22	<2.5	0.1	3.4	5.33	90
CM9-33	3/31/2001	796.44 E	15.53	<5	<5	ND	ND	ND	0.68	0.60	<39.8	0.01	18.51	1.80	ND	<2.5	0.1	0.9	5.4	74
CM9-33D	3/31/2001	589.22	16.86	<5	<5	ND	ND	ND	ND	ND	<34.2	ND	ND	ND	ND	ND	ND	ND	ND	ND
CM10-0.5	3/29/2001	1.73	0.45	ND	ND	<5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CM10-12	3/29/2001	30.95	3.59	ND	ND	ND	ND	ND	5.73	5.64	623	0.11	12.78	3.96	16	<2.5	0.3	3.0	5.79	75
CM10-20	3/29/2001	86.98	13.53	<5	<5	ND	ND	<5	5.17	5.20	299	<0.1	13.97	2.65	10	<2.5	0.2	6.1	6.02	104
CM11-1T	3/29/2001	3.12	1.05	ND	<5	ND	ND	<5	ND	ND	<35.8	<0.1	ND	ND	27	ND	ND	ND	ND	ND
CM11-12	3/29/2001	ND	ND	ND	ND	ND	ND	ND	2.95	2.85	62	<0.1	16.96	2.85	10	<2.5	<0.1	2.6	5.53	77
CM11-20	3/29/2001	64.2	7.74	<5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CM12-1T	3/29/2001	4.16	ND	ND	ND	ND	ND	ND	0.73	0.73	<46.2	ND	15.39	2.74	9	<2.5	<0.1	6.3	5.74	85
CM12-12	3/31/2001	274.44	19.6	ND	ND	ND	ND	1.43	2.72	2.66	<39.8	0.01	15.39	2.74	9	<2.5	<0.1	6.3	5.74	85
CM12-23	4/4/2001	816.93 E	15.19	<5	<5	ND	ND	ND	2.27	2.26	<37.8	0.03	18.62	2.18	ND	<2.5	<0.1	2.2	5.68	99
CM12-23D	4/4/2001	818.44 E	15.18	<5	<5	ND	ND	ND	2.32	2.26	ND	ND	ND	ND	ND	<2.5	0.1	ND	ND	ND
CM12-23D	4/4/2001	611.24	16.36	<5	0.48	<5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CM13-1T	4/3/2001	96.00	72.4	0.59	<5	ND	ND	ND	0.77	0.75	90	0.06	16.08	3.14	40	ND	ND	ND	ND	ND
CM13-1T	3/31/2001	26.82	<5	ND	<5	ND	ND	<5	0.13	0.14	<39.5	<0.1	10.55	2.97	6	<2.5	0.6	4.2	4.25	51
CM13-2T	3/31/2001	269.68	5.8	<5	<5	ND	ND	0.52	0.02	0.05	<31.2	<0.1	31.30	3.38	ND	<2.5	<0.1	2.6	4.72	76
CM13-12	3/31/2001	274.44	5.8	<5	<5	ND	ND	1.73	0.87	0.86	<39.4	0.15	32.12	2.86	7	<2.5	0.1	2.3	5.48	123
CM13-21	3/31/2001	204.9	3.69	ND	ND	ND	ND	2.26	0.44	0.41	<36.9	<0.1	21.26	4.65	ND	<2.5	<0.1	2.2	5.63	93
CM14-2T	3/31/2001	<5	ND	ND	<5	ND	ND	<5	3.41	3.37	43	0.19	10.87	3.66	8	<2.5	0.1	0.4	5.06	43
CM14-5	3/31/2001	<5	ND	ND	<5	ND	ND	ND	4.76	4.60	66	0.19	16.18	2.60	12	<2.5	1	1.4	5.28	66
CM15-1T	3/30/2001	<5	ND	<5	<5	ND	ND	ND	ND	ND	837	ND	ND	4.83	22	ND	ND	ND	ND	ND
CM15-12	3/30/2001	ND	ND	<5	<5	ND	ND	ND	2.51	2.49	566	0.01	10.27	3.49	6	<2.5	0.1	7.3	5.59	129
CM16-1T	4/4/2001	0.73	ND	ND	ND	ND	ND	ND	ND	ND	<47.5	ND	ND	ND	ND	ND	ND	ND	ND	ND
CM16-10	3/30/2001	12.2	1.03	ND	ND	ND	ND	ND	6.13	6.07	156	<0.1	9.09	3.03	2	<2.5	<0.1	7.5	5.85	47
CM16-28	3/30/2001	344.84 E	15.85	<5	<5	ND	ND	<5	3.79	3.77	113	0.03	16.30	1.85	8	<2.5	0.4	1.1	6.38	54
CM16-28D	3/30/2001	320.32	16.15	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CM17-0.5T	3/30/2001	0.66	ND	ND	<5	ND	ND	ND	4.51	4.91	241	0.22	3.62	2.79	3	ND	ND	ND	6.13	42
CM17-12	4/5/2001	ND	ND	ND	<5	ND	ND	ND	4.71	4.70	89	0.02	ND	ND	ND	ND	ND	ND	6.0	89
CM17-23	3/30/2001	308.98 E	8.16	<5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Well	Date Collected	TCE (ug/L)	c12DCE (ug/L)	112DCE (ug/L)	VC (ug/L)	Benzene (ug/L)	p-Isopropyl- toluene (ug/L)	Toluene (ug/L)	FeTot (ppm)	Fe2+ (ppm)	CH4 (ug/L)	Sulfide (ppm)	Sulfate, Chloride, Dissolved (mg/L)		DOC (mg/L)	Nitrate (mg/L)	Ammonia (mg/L)	Dissolved Oxygen (mg/L)	pH	Specific Cond. (uS/cm)
CM17-23	3/30/2001	264.86	8.34	<5	<5	N.D.	N.D.	N.D.	1.81	1.77	<31.5	<0.1	7.96	2.73	7	<2.5	0.4	3.1	5.08	37
CM17-51	3/30/2001	0.54	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.81	1.77	<31.5	<0.1	7.96	2.73	7	<2.5	0.4	3.1	5.08	37
CM18-16	3/31/2001	1.58	N.D.	N.D.	<5	N.D.	N.D.	N.D.	1.81	1.77	<31.5	<0.1	7.96	2.73	7	<2.5	0.4	3.1	5.08	37
CM18-55	4/5/2001	1.58	N.D.	N.D.	<5	N.D.	N.D.	N.D.	1.81	1.77	<31.5	<0.1	7.96	2.73	7	<2.5	0.4	3.1	5.08	37
STREAM PIEZOMETERS																				
ST1-1	4/2/2001	281.4	1.56	N.D.	N.D.	N.D.	N.D.	N.D.	0.01	0.02	<41.8	0.02	6.89	4.09	5	<2.5	--	1.8	4.7	44
ST1-3	4/2/2001	278.65	1.52	N.D.	<5	N.D.	N.D.	N.D.	0.01	<0.01	<38.3	0.01	6.42	4.68	21	--	--	2.0	5.15	45
ST2-1	4/3/2001	391.36 E	28.11	<5	N.D.	N.D.	N.D.	N.D.	0.15	0.10	<35.5	0.01	14.37	2.30	9	<2.5	<0.1	1.0	4.68	65
ST2-10	4/3/2001	320.98	26.99	0.45	<5	N.D.	N.D.	N.D.	0.17	0.16	<56.0	0.05	13.74	2.17	--	<2.5	<0.1	--	4.62	49
ST2-3	4/3/2001	465.87 E	43.23	0.63	<5	N.D.	N.D.	N.D.	0.17	0.16	<56.0	0.05	13.74	2.17	--	<2.5	<0.1	--	4.62	49
ST2-3D	4/3/2001	323.64	33.86	<5	<5	N.D.	N.D.	N.D.	0.03	<0.01	<36.8	<0.1	11.69	2.52	8	--	--	1.3	5.15	46
ST3-1	4/5/2001	137.52	7.22	0.17	<5	N.D.	N.D.	N.D.	0.03	<0.01	<36.8	<0.1	11.69	2.52	8	--	--	1.3	5.15	46
ST3-4	4/5/2001	126.46	3.78	N.D.	<5	N.D.	N.D.	N.D.	<0.01	<0.01	<34.7	0.02	8.18	2.18	3	--	--	3.2	4.80	38
ST4-1	4/3/2001	18.81	6.43	N.D.	<5	N.D.	N.D.	N.D.	0.10	0.10	<39.4	0.05	5.92	3.11	16	<2.5	<0.1	1.8	4.89	32
ST4-2	3/31/2001	N.D.	N.D.	N.D.	<5	N.D.	N.D.	N.D.	0.04	0.05	<45.0	<0.1	1.79	2.98	21	<2.5	<0.1	1.3	4.90	48
ST4-3	3/31/2001	N.D.	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	--	<31.8	<0.1	1.61	3.45	7	<2.5	0.2	--	5.02	48
ST5-3	4/3/2001	12.87	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.06	0.01	<33.3	<0.1	27.74	2.72	21	<2.5	<0.1	4.2	4.78	112
ST5-3D	4/3/2001	12.27	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.52	0.52	513	0.5	47.48	5.37	8	<2.5	0.3	2.1	4.82	83
ST6-3	4/2/2001	2.47	3.05	N.D.	<5	N.D.	N.D.	<5	0.63	0.63	294	1.04	21.49	4.28	4	<2.5	0.3	0.3	5.52	77
SWB-1T	4/2/2001	5.81	1.04	N.D.	<5	N.D.	N.D.	N.D.	0.44	0.48	42	0.22	46.02	6.80	9	--	--	2.8	5.16	127
SURFACE WATERS																				
S9	4/3/2001	68.06	1.89	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	12.21	2.56	11	--	--	--	4.01	64
S10	4/5/2001	13.74	<5	N.D.	<5	N.D.	N.D.	N.D.	--	--	--	--	10.13	3.85	3	--	--	6.2	4.93	52
S11	2001	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
S13	4/3/2001	16.39	0.48	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	9.36	3.71	38	--	--	7.0	4.20	52
S14	4/3/2001	20.39	0.46	N.D.	<5	N.D.	N.D.	N.D.	--	--	--	--	10.20	3.72	11	--	--	7.3	4.05	53
S14D	4/3/2001	17.89	0.59	N.D.	<5	N.D.	N.D.	N.D.	--	--	--	--	10.95	4.45	3	--	--	4.19	53	
S15	4/3/2001	17.76	0.47	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	<42.3	<0.1	9.91	3.42	3	--	--	7.1	4.10	51
S16	4/2/2001	0.33	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.22	0.24	<42.3	<0.1	8.78	3.80	7	--	--	6.9	4.47	44
S20	2001	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
S21	2001	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
SWB-Surf Water	4/2/2001	0.84	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.33	<0.01	<35.6	<0.1	9.25	3.21	4	<2.5	0.3	6.7	4.38	46
Quality Assurance Samples-Wash Blanks																				
Wash Blank after S16	4/2/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<5	--	--	--	--	0.08	0.04	5	--	--	--	--	--
Wash Blank after CM7-12	4/3/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<5	--	--	--	--	0.00	0.00	1	--	--	--	--	--
Wash Blank after CM5-1.6	4/2/2001	0.71	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	-0.06	-0.01	8	--	--	--	--	--
Wash Blank after CM9-5	4/4/2001	<5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	0.00	0.00	0	--	--	--	--	--
Wash Blank after CM12-23	4/4/2001	0.64	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	0.00	0.00	--	--	--	--	--	--
Wash Blank after CM12-23	4/4/2001	0.63	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	--	--	--	--	--	--	--	--	--	--	--
Wash Blank after CM13-2	4/4/2001	<5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	--	--	--	--	--	--	--	--
Wash Blank after CM16-10	3/30/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	0.00	0.19	4	--	--	--	--	--
PEEPERS																				
PCM3-8	4/4/2001	<5	N.D.	N.D.	N.D.	0.78	N.D.	N.D.	--	--	<50.8	--	--	--	--	--	--	--	--	0.75
PCM3-9	4/4/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	--	--	--	--	--	--	--	3.75
PCM3-10	4/4/2001	N.D.	N.D.	N.D.	<5	N.D.	N.D.	N.D.	0.86	64	69	0.01	--	--	--	--	--	--	--	6.75
PCM3-11	4/4/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	1.99	69	0.62	--	--	--	--	--	--	--	9.75
PCM3-12	4/4/2001	N.D.	<5	N.D.	N.D.	<5	N.D.	0.67	--	5.56	1067	--	--	--	--	--	--	--	--	12.75
PCM3-13	4/4/2001	N.D.	1.68	N.D.	<5	N.D.	N.D.	1.75	--	7.59	3064	0.33	--	--	--	--	--	--	--	15.75
PCM3-14	4/4/2001	N.D.	2.75	N.D.	N.D.	<5	N.D.	1.68	--	11.64	3808	0.13	--	--	--	--	--	--	--	18.75
PCM3-15	4/4/2001	N.D.	2.76	N.D.	N.D.	<5	N.D.	0.84 E	--	10.34	3664	0.31	--	--	--	--	--	--	--	24.75
PCM3-16	4/4/2001	0.5	1.92	N.D.	<5	N.D.	N.D.	<5	--	10.99	3079	0.06	--	--	--	--	--	--	--	30.75
PCM3-17	4/4/2001	0.66	1.19	N.D.	<5	0.77 E	N.D.	<5	--	10.50	2728	0.14	--	--	--	--	--	--	--	33.75
PCM3-18	4/4/2001	1.12	0.92	N.D.	<5	0.52 E	N.D.	<5	--	9.78	2238	0.22	--	--	--	--	--	--	--	39.75
PCM3-19	4/4/2001	1.39	1.07	N.D.	N.D.	<5	N.D.	0.65	--	16.83	--	--	--	--	--	--	--	--	--	30.75
PCM3-20	4/4/2001	1.32	0.97	N.D.	<5	1.53 E	N.D.	<5	--	7.18	1249	0.43	--	--	--	--	--	--	--	33.75
PCM3-21	4/4/2001	0.68	0.58	N.D.	N.D.	1.35 E	N.D.	<5	--	5.64	512	1.15	--	--	--	--	--	--	--	39.75
PEEPERS																				
PCM8-1	4/4/2001	0.45	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	0.33	<56.7	<0.1	--	--	--	--	--	--	--	0.75
PCM8-2	4/4/2001	N.D.	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	0.33	<91.5	<0.1	--	--	--	--	--	--	--	3.75
PCM8-3	4/4/2001	<5	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	0.57	<80.3	--	--	--	--	--	--	--	--	6.75
PCM8-4	4/4/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	1.30	<60.8	<0.1	--	--	--	--	--	--	--	9.75
PCM8-5	4/4/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	3.98	<57.9	0.02	--	--	--	--	--	--	--	12.75
PCM8-6	4/4/2001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	6.44	<74.6	<0.1	--	--	--	--	--	--	--	15.75
PCM8-7	4/4/2001	N.D.	<5	N.D.	N.D.	<5	N.D.	N.D.	--	5.24	<69.2	0.02	--	--	--	--	--	--	--	18.75
PCM8-8	4/4/2001	<5	1.74	N.D.	<5	N.D.	N.D.	N.D.	--	5.64	77	0.08	--	--	--	--	--	--	--	21.75
PCM8-9	4/4/2001	N.D.	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	6.36	136	0.13	--	--	--	--	--	--	--	24.75
PCM8-10	4/4/2001	N.D.	5.13	N.D.	<5	N.D.	N.D.	N.D.	--	6.52	238	<0.1	--	--	--	--	--	--	--	27.75
PCM8-11	4/4/2001	N.D.	4	N.D.	<5	N.D.	N.D.	N.D.	--	8.04	484	0.27	--	--	--	--	--	--	--	30.75
PCM8-12	4/4/2001	N.D.	16.73	0.57	<5	0.62	N.D.	N.D.	--	11.81	801	0.14	--	--	--	--	--	--	--	33.75
PCM8-13	4/4/2001	N.D.	6.57	<5	<5	N.D.	N.D.	N.D.	--	10.77	823	0.14	--	--	--	--	--	--	--	36.75
PCM8-14	4/4/2001	N.D.	23.63	0.52	<5	0.64	N.D.	N.D.	--	10.85	676	0.15	--	--	--	--	--	--	--	39.75
PCM8-15	4/4/2001	N.D.	45.54	0.62	<5	N.D.	N.D.	N.D.	--	10.93	749	0.22	--	--	--	--	--	--	--	42.75
PCM8-16	4/4/2001	<5	51.54	0.59	<5	N.D.	N.D.	N.D.	--	10.52	858	0.32	--	--	--	--	--	--	--	45.75

Well	Date Collected	TCE (µg/L)	c12DCE (µg/L)	12DCE (µg/L)	VC (µg/L)	Benzene (µg/L)	p-Isopropyl-toluene (µg/L)	Toluene (µg/L)	FeTot (ppm)	Fe2+ (ppm)	CH4 (µg/L)	Sulfide (ppm)	Dissolved Sulfate (mg/L)	Chloride, Dissolved (mg/L)	DOC (mg/L)	Nitrate (mg/L)	Ammonia (mg/L)	Dissolved Oxygen (mg/L)	pH	Specific Cond. (µS/cm)
PCM9-17	4/4/2001	N.D.	28.97	<5	<5	1.07	N.D.	N.D.	--	11.49	1082	0.38	--	--	--	--	--	--	--	48.75
PCM9-18	4/4/2001	N.D.	29.99	0.76	<5	<5	N.D.	N.D.	--	11.57	1043	0.27	--	--	--	--	--	--	--	51.75
PCM9-19	4/4/2001	N.D.	31.29	0.78	<5	<5	N.D.	N.D.	--	13.09	1020	0.74	--	--	--	--	--	--	--	54.75
PCM9-20	4/4/2001	0.51	49.51	0.88	<5	1.4	N.D.	N.D.	--	16.05	995	1.12	--	--	--	--	--	--	--	57.75
PCM9-21	4/4/2001	1.35	61.31	1.24	<5	<5	N.D.	N.D.	--	17.49	850	0.27	--	--	--	--	--	--	--	60.75
PCM13-1	4/4/2001	6.45	3.77	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	63	--	--	--	--	--	--	--	--	0.75
PCM13-2	4/4/2001	12.31	6.1	N.D.	<5	N.D.	N.D.	N.D.	--	--	131	--	--	--	--	--	--	--	--	3.75
PCM13-3	4/4/2001	6.71	8.72	<5	<5	N.D.	N.D.	N.D.	--	0.72	143	0.18	--	--	--	--	--	--	--	6.75
PCM13-4	4/4/2001	3.88	8.5	N.D.	<5	<5	N.D.	N.D.	--	1.12	121	0.45	--	--	--	--	--	--	--	9.75
PCM13-5	4/4/2001	3.58	8.38	N.D.	<5	N.D.	N.D.	N.D.	--	1.28	109	0.60	--	--	--	--	--	--	--	12.75
PCM13-6	4/4/2001	3.57	6.91	N.D.	<5	N.D.	N.D.	N.D.	--	1.92	131	--	--	--	--	--	--	--	--	15.75
PCM13-7	4/4/2001	7.01	5.86	N.D.	<5	0.49	N.D.	N.D.	--	2.16	103	0.64	--	--	--	--	--	--	--	18.75
PCM13-8	4/4/2001	9.52	3.98	N.D.	<5	0.49	N.D.	N.D.	--	2.00	<53.2	0.36	--	--	--	--	--	--	--	21.75
PCM13-9	4/4/2001	9.12	3.02	N.D.	<5	0.24	N.D.	N.D.	--	2.00	<62.7	0.67	--	--	--	--	--	--	--	24.75
PCM13-10	4/4/2001	10.37	2.99	N.D.	N.D.	0.54	N.D.	N.D.	--	1.80	<62.4	0.24	--	--	--	--	--	--	--	27.75
PCM13-11	4/4/2001	10.99	3.38	N.D.	<5	N.D.	N.D.	N.D.	--	1.60	91	0.07	--	--	--	--	--	--	--	30.75
PCM13-12	4/4/2001	10.21	3.09	N.D.	<5	N.D.	N.D.	N.D.	--	1.60	91	0.17	--	--	--	--	--	--	--	33.75
PCM13-13	4/4/2001	10.99	2.12	N.D.	<5	<5	N.D.	N.D.	--	3.20	176	0.52	--	--	--	--	--	--	--	36.75
PCM13-14	4/4/2001	13.25	3.68	<5	<5	0.95	N.D.	N.D.	--	3.20	176	0.52	--	--	--	--	--	--	--	39.75
PCM13-15	4/4/2001	40.58	3.81	0.06	<5	0.95	N.D.	N.D.	--	1.36	88	0.38	--	--	--	--	--	--	--	42.75
PCM13-16	4/4/2001	15.28	3.47	N.D.	N.D.	N.D.	N.D.	N.D.	--	1.52	<78.2	0.31	--	--	--	--	--	--	--	45.75
PCM13-17	4/4/2001	11.12	3	N.D.	N.D.	<5	N.D.	N.D.	--	1.60	<64.0	0.09	--	--	--	--	--	--	--	48.75
PCM13-18	4/4/2001	16.94	4.83	<5	N.D.	<5	N.D.	N.D.	--	1.92	<65.9	0.32	--	--	--	--	--	--	--	51.75
PCM13-19	4/4/2001	16.67	3.91	<5	<5	<5	N.D.	N.D.	--	2.32	<75.7	0.29	--	--	--	--	--	--	--	54.75
PCM13-20	4/4/2001	21.77	5.34	<5	<5	<5	<5	N.D.	--	1.36	<78.9	0.21	--	--	--	--	--	--	--	57.75
PCM13-21	4/4/2001	70.22	9.39	<5	<5	N.D.	N.D.	N.D.	--	--	<54.7	0.18	--	--	--	--	--	--	--	60.75
PLST4-5	4/4/2001	0.72	N.D.	N.D.	N.D.	<5	N.D.	N.D.	--	0.09	<55.6	<0.1	9.70	3.13	10	--	--	--	--	0.98
PLST4-6	4/4/2001	3.95	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	0.09	<48.7	0.01	9.35	3.18	1	--	--	--	--	6.46
PLST4-7	4/4/2001	15.65	<5	N.D.	<5	N.D.	N.D.	N.D.	--	<0.01	<49.0	0.03	--	--	--	--	--	--	--	11.95
PLST4-8	4/4/2001	16.16	0.57	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	--	--	--	--	--	--	--	17.43
PLST4-9	4/4/2001	8.72	<5	N.D.	<5	N.D.	N.D.	N.D.	--	0.09	<49.2	0.01	8.31	3.32	6	--	--	--	--	22.92
PLST4-10	4/4/2001	4.73	<5	N.D.	N.D.	N.D.	N.D.	N.D.	--	--	--	--	--	--	--	--	--	--	--	28.41
PLST4-11	4/4/2001	4.87	<5	N.D.	<5	N.D.	N.D.	N.D.	--	0.09	<49.8	<0.1	10.33	3.52	4	--	--	--	--	33.89
PLST4-12	4/4/2001	4.29	0.47	N.D.	<5	N.D.	N.D.	N.D.	--	0.81	<57.0	0.04	--	--	--	--	--	--	--	39.38
PLST4-13	4/4/2001	2.53	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	2.10	<41.8	0.06	5.11	2.74	6	--	--	--	--	44.86
PLST4-14	4/4/2001	1.18	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	1.54	<52.9	0.06	6.36	3.37	11	--	--	--	--	50.35
PLST4-15	4/4/2001	0.86	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	1.38	<62.5	0.03	--	--	--	--	--	--	--	55.84
PLST4-16	4/4/2001	1.18	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	0.97	<50.7	0.10	3.62	2.68	4	--	--	--	--	61.32
PLST4-17	4/4/2001	0.68	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	1.36	<42.5	0.04	5.06	2.87	1	--	--	--	--	66.81
PLST4-18	4/4/2001	0.73	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	0.81	<57.3	0.08	--	--	--	--	--	--	--	72.29
PLST4-19	4/4/2001	1.34	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	--	0.25	<39.4	0.18	4.06	2.81	4	--	--	--	--	77.76
PLST4-20	4/4/2001	0.69	N.D.	N.D.	<5	N.D.	N.D.	N.D.	--	0.09	<43.4	0.09	4.74	2.91	5	--	--	--	--	83.27
PLST4-21	4/4/2001	0.83	N.D.	N.D.	<5	<5	N.D.	N.D.	--	0.17	<45.7	0.33	5.76	2.99	7	--	--	--	--	88.75
PLST4-22	4/4/2001	0.63	<5	N.D.	<5	N.D.	N.D.	N.D.	--	<0.01	<58.0	0.08	5.25	2.80	--	--	--	--	--	94.24

CM18 Sediment Core; 12/11/00; **Lorah** (anyone else?)

GPS Reading: none

Depth, refers to the bottom of the specified interval; alphanumeric codes at selected horizons refer to color designations as specified in the Munsell

Soil Color Charts (1975), example (2.5Y-3/1)

Type of core?

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)
Peat, dark brown to black	0.33	0.33	0-4
Soft clay, black	0.58	0.25	0-4
Sand, coarse, grey, 2.5Y-6/1	2.00	1.42	0-4
Sand, coarse, very dark brown, 10YR-2/2	2.42	0.42	0-4
Sand, coarse, silty, dark reddish brown, very wet, smelled sulfur, 5YR-4/2	3.25	0.83	0-4
Sand, coarse, coarse, very dark, smelled sulfur, 10YR-2/2	4.00	0.75	0-4
Sand, coarse, very dark brown, 10YR-2/2	6.17	2.17	4-8
Sand, very coarse, clean, brown, 10YR-5/3	8.00	1.83	4-8
Sand, medium-coarse, brownish-yellow, thin black laminations alternating with white sand (10YR-8/1), 10YR-6/6, 3.2' recovery	12.00	4.00	8-12
Sand, medium-coarse, black laminations about 3mm thick and also have a rust color mixed in with black, some 5mm-sized angular to sub-rounded gravel, more gravel in top 0.5' than elsewhere, brownish-yellow, 10YR-6/6, 3.3' recovery	16.00	4.00	12-16
Sand, fine-medium, clean, same as above but no gravel, 10YR-6/6, 2.7' recovery	20.00	4.00	16-20
Sand, fine-medium, a little silty, 1 piece of gravel, clean, black laminations, 10YR-6/6, 2.4' recovery	24.00	4.00	20-24
Sand, medium-coarse, silty, small lenses of dark red silt and fine sand (2.5YR-4/8), 5YT-5/8, 0.5' recovery	28.00	4.00	24-28
Sand, medium-coarse, clean, a few pieces angular 5mm-sized gravel, yellowish-red, 5YR-5/8	29.65	1.65	28-32
Sand, medium-coarse, silty, small angular gravel, reddish-yellow, 7.5YR-6/8	30.20	0.55	28-32
Sand, medium-coarse, angular gravel to 10mm size, pale yellow, 2.5Y-8/3	31.80	1.6	28-32
No Recovery	32.00	0.2	28-32

End of coring

SS1 Sediment Core; located at Lakehurst side of Collier Mills on north side of dirt road a few hundred feet east of fire pond; 2/26-27/01; Phelan and Dyer

GPS Reading: N 40 02.083, W 74 25.621

Depth, refers to the bottom of the specified interval; alphanumeric codes at selected horizons refer to color designations as specified in the Munsell Soil Color Charts (1975), example (2.5Y-3/1)

Cores were taken from 2 ft-long split-spoon barrels

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)
Sand, fine-medium, light gray, 5YR-6/1	0.65	0.65	0-2
Sand, fine-medium, poorly-sorted, yellow-brown, 10YR-4/5	0.85	0.2	0-2
Sand, fine-medium, poorly-sorted, light yellow-brown, 10YR-6/6	1.5	0.65	0-2
Sand, medium, poorly-sorted, beige, 10YR-5/4	3.0	1.0	2-4
Sand, coarse with 1/16" to 1/2" gravel, beige, 10YR-5/4	3.5	0.5	2-4
Sand, coarse with 1/8" to 1/2" gravel, yellow-brown, 10YR-6/6	4.0	0.5	2-4
Sand, medium, brown, 10YR-4/4	4.3	0.3	4-6
Sand, medium-coarse, yellow-orange, 7.5YR-6/6	4.4	0.1	4-6
Sand, medium-coarse, yellow, 10YR-7/6	6.0	1.6	4-6
Sand, medium, brown, 10YR-4/4	6.2	0.2	6-8
Sand, medium-coarse, yellow-orange, 10YR-7/6	7.0	0.8	6-8
Sand, medium-coarse, yellow-beige, 10YR-7/3	8.0	1.0	6-8
Sand, coarse, poorly-sorted, yellow-orange, 10YR-7/6	8.5	0.5	8-10
Sand, medium-coarse, poorly-sorted, occasional small quartz pebbles, beige, 2.5Y-7/4	10.0	1.5	8-10
Sand, medium, dark laminations at 10.6'-11.0', beige, 10YR-3/1	12.0	2.0	10-12
Sand, medium, yellow-beige, 2.5Y-7/3	12.1	0.1	12-14
Sand, medium-coarse, poorly-sorted, occasional quartz pebbles, tan, 10YR-6/5	12.4	0.3	12-14
Sand, medium-coarse, tan, 10YR-5/5	12.7	0.3	12-14
Sand, medium-coarse, dark brown, 10YR-3/4	12.75	0.1	12-14
Sand, medium-coarse, red, 2.5YR-4/5	13.0	0.3	12-14
No Recovery	14.0	1.0	12-14
Sand, medium-coarse, iron-cemented nodules from 0.02'-0.04', red, 2.5YR-4/4	14.6	0.6	14-16
Sand, medium-coarse, 0.05' band of red, poorly-sorted med-coarse sand at 14.75', orange-tan, 10YR-6/5	15.0	0.4	14-16
No Recovery	16.0	1.0	14-16
Sand, fine-medium, occasional dark-brown thin bands, yellow-brown, 2.5Y-5/4	17.0	1.0	16-18
No Recovery	18.0	1.0	16-18
Sand, medium, well-sorted, contains dark brown laminations that are 2.5Y-3/3, yellow-brown, 2.5Y-5/4	18.3	0.3	18-20
Sand, fine-medium, yellowish-beige, 2.5Y-6/6	18.4	0.1	18-20
Sand, medium, well-sorted, contains dark brown laminations that are 2.5Y-3/3, yellow-brown, 2.5Y-5/4	18.6	0.2	18-20
Silt, two very thin layers about 1/2" apart, white-cream, 2.5Y-8/2	18.65	0.05	18-20
Sand, medium, well-sorted, contains dark brown laminations that are 2.5Y-3/3, yellow-brown, 2.5Y-5/4	18.9	0.3	18-20
Sane, fine-medium, yellow-brown, 2.5Y-5/5	19.0	0.1	18-20
No Recovery	20.0	1.0	18-20

Generally medium-grained sands  
varying in color from beige to pi  
to red to yellow to orange  
**Cohansey Formation**

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)
Sand, fine-medium, yellow-brown, 2.5Y-6/5	20.3	0.3	20-22
Sand, fine-medium, dark brown, 10YR-3/5	20.35	0.05	20-22
Sand, fine-medium, tan, (contains two dark brown bands at 20.6' and 20.7'), 2.5Y-5/4	20.9	0.5	20-22
No Recovery	22.0	1.1	20-22
Silt, very thin layer, white-cream, 2.5Y-8/2	22.05	0.05	22-24
Sand, fine-medium, yellow-beige (contains several 1/2" bands of 10YR-6/5 fine-medium sand), 2.5Y-6/4	22.6	0.55	22-24
Sand, medium-coarse, occasional small quartz pebbles, orange-beige, 10YR-6/6	23.0	0.4	22-24
No Recovery	24.0	1.0	22-24
Sand, medium-coarse, poorly sorted, brown-orange (contains two small bands of dark brown 10YR-3/4), 10YR-5/4 to 5/6	24.9	0.9	24-26
Sand, fine-medium, contains some silt, orange, 7.5YR-6/6	25.0	0.1	24-26
No Recovery	26.0	1.0	24-26
Sand, fine-medium, orange, 7.5YR-6/6	26.8	0.8	26-28
Sand, fine-medium, brown-orange, 10YR-5/6	27.0	0.2	26-28
No Recovery	28.0	1.0	26-28
Sand, fine-medium, yellow-tan, (contains occasional dark brown 2.5Y-4/4 bands/swirls), 2.5Y-5/5	29.1	1.1	28-30
No Recovery	30.0	0.9	28-30
Sand, medium-coarse, beige, 2.5Y-6/4	30.4	0.4	30-32
Sand, fine-medium, orange-brown, (contains a few 10YR-3/4 brown bands), 7.5YR-5/6	30.7	0.3	30-32
Sand, fine-medium, well sorted, tan, 10YR-5/6	30.9	0.2	30-32
Sand, fine-medium, well sorted, yellow-tan, 2.5Y-6/5	31.1	0.2	30-32
No Recovery	32.0	0.9	30-32
Sand, medium-coarse, beige, 10YR-6/3	32.6	0.6	32-34
Sand, medium-coarse, dark yellow-tan, 5YR-5/5	32.9	0.3	32-34
Sand, medium-coarse, yellow-tan, 5YR-6/4	33.3	0.4	32-34
No Recovery	34.0	0.7	32-34
Sand, medium-coarse, orange, 5YR-6/5	34.2	0.2	34-36
Sand, coarse, poorly-sorted, angular quartz fragments, gradual change from beige to orange-pink, 10YR-6/3 to 5YR-6/5	34.9	0.7	34-36
Sand, fine-medium, well sorted, yellow-tan, 2.5Y-6/4	35.3	0.4	34-36
No Recovery	36.0	0.7	34-36
Sand, fine-medium, yellowish-beige, mottled, 10YR-6/5 and 10YR-7/4	36.5	0.5	36-38
Sand, medium, beige, 2.5Y-7/3	36.8	0.3	36-38
Sand, medium, beige, 2.5Y-7/3 with yellowish 7.5YR-5/6 mottles throughout	37.7	0.9	36-38
No Recovery	38.0	0.3	36-38
Sand, medium-coarse, contains some small quartz pebbles, gradual change from pinkish-beige to yellowish-beige, 10YR-6/4 to 7.5YR-5/5	39.0	1.0	38-40
Sand, medium-coarse, beige and pinkish-beige, 7.5YR-7/4	39.5	0.5	38-40
No Recovery	40.0	0.5	38-40
Sand, fine-medium, fairly well-sorted, zoned colors, orange-red and beige, 7.5YR-5/6 to 10YR-7/3	41.7	1.7	40-42

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)
Sand, medium-coarse, fairly well-sorted, zoned colors, orange-red and beige, 7.5YR-5/6 to 10YR-6/6	41.9	0.2	40-42
Sand, medium-coarse, orange-red, 10YR-7/3	42.0	0.1	40-42
Sand, medium-coarse, orange-red, 10YR-7/3	42.4	0.4	42-44
Sand, fine-medium, red-orange, 7.5YR-6/6	42.6	0.2	42-44
Sand, fine-medium, red-orange, 10YR-7/6	42.9	0.3	42-44
Sand, fine-medium, orange-beige to beige, 2.5Y-7/2	43.3	0.4	42-44
No Recovery	44.0	0.7	42-44
Sand, medium-coarse, several small quartz pebbles, yellowish-beige, 2.5Y-6/4	44.5	0.5	44-46
Sand, medium, yellowish-beige, 2.5Y-6/5	44.9	0.4	44-46
Sand, fine-medium, well-sorted, beige, 2.5Y-7/1	45.3	0.4	44-46
Sand, fine-medium, well-sorted, yellowish-beige, 2.5Y-6/5	45.6	0.3	44-46
No Recovery	46.0	0.4	44-46
Sand, medium-coarse, light yellowish-beige, 2.5Y-6/3	46.4	0.4	46-48
Sand, medium-coarse, fines downward to fine-medium sand at 47.6' and becomes more well-sorted, gradual color change from yellowish-beige to beige, 2.5Y-6/5 to 2.5Y-7/4	47.6	1.2	46-48
No Recovery	48.0	0.4	46-48
Sand, medium, light yellowish-beige, 2.5Y-6/4 with some darker mottles of 2.5Y-5/4 from 48.6' to 49.0'	49.0	1.0	48-50
Sand, fine-medium, (contains 0.1' band of fine-medium very light beige 2.5Y-5/4), yellowish-beige, 2.5Y-7/2	49.4	0.4	48-50
No Recovery	50.0	0.6	48-50
Sand, fine-medium, yellowish-beige, 2.5Y-7/3	50.7	0.7	50-52
Sand, fine-medium, yellowish-beige, 2.5Y-7/5	50.9	0.2	50-52
Sand, fine-medium, yellowish-beige, 2.5Y-7/3	51.1	0.2	50-52
Sand, fine-medium, yellowish-beige, 2.5Y-7/5	51.3	0.2	50-52
Sand, fine-medium, yellowish-beige, 2.5Y-7/3	51.7	0.4	50-52
No Recovery	52.0	0.3	50-52
Sand, fine-medium, yellowish-beige, 2.5Y-6/4	52.5	0.5	52-54
Sand, fine-medium, (contains thin layer of white silt with 2.5Y-6/5 fine sand on either side), orange-beige, 2.5Y-7/3	52.7	0.2	52-54
Sand, fine-medium, light orange-red, ranges from 7.5YR-6/4 at top of interval to 7.5YR-5/5 at bottom of interval	53.1	0.4	52-54
Sand, fine-medium, orange-beige, 10YR-5/4	53.4	0.3	52-54
No Recovery	54.0	0.6	52-54
Sand, fine-medium, (contains two bands of fine-medium sand, 10YR-6/6 at 54.4 and 54.6'; the lower band contains a thin white layer of silt), yellowish-tan, 10YR-4/5	55.0	1.0	54-56
Sand, medium-coarse, beige, 2.5Y-6/4	55.4	0.4	54-56
No Recovery	56.0	0.6	54-56
Sand, medium-coarse, light orange-yellow, 2.5Y-6/5	56.2	0.2	56-58
Sand, fine-coarse, poorly sorted, thin layer of clayey silt (2.5Y-8/1) at 56.3', orange-beige, 7.5YR-6/6	56.3	0.1	56-58



Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)
Sand, fine-medium, yellowish-beige, 2.5Y-7/5	56.7	0.4	56-58
Sand, fine, contains thin laminations of 10YR-6/6 fine sand and clay, yellowish-beige, 2.5-7/5	56.9	0.2	56-58
Sand, coarse, orange-beige, 2.5Y-7/2	57.0	0.1	56-58
Sand, fine-coarse, poorly-sorted, contains thin laminations of white silty clay at 57.3', orange-beige, 10YR-6/6	57.4	0.4	56-58
No Recovery	58.0	0.6	56-58
Sand, medium-coarse, poorly-sorted, orange to orange-pink, 7.5YR-6/6	58.4	0.4	58-60
Sand, coarse, poorly-sorted, band of well-sorted medium sand (2.5Y-6/5) at 58.7', light yellowish-beige, 2.5Y-7/4	59.4	1.0	58-60
No Recovery	60.0	0.6	58-60
Sand, coarse, yellowish-beige, 2.5Y-6/5	60.6	0.6	60-62
Sand, fine-medium, fines downward, contains a thin clayey-silt layer at 60.9', orange-yellow, 7.5YR-5/6	61.1	0.5	60-62
Sand, fine-medium, well-sorted, contains a 1/2" clayey-silt layer at 61.3', light pinkish-orange, 10YR-6/6	61.3	0.2	60-62
No Recovery	62.0	0.7	60-62
Sand, medium-coarse, occasional small quartz pebbles, thin silty layers at 62.5' and 62.6', yellow and orange, 10YR-6/6	63.4	1.4	62-64
No Recovery	64.0	0.6	62-64
Sand, fine, contains thin silty layer at 64.1' and a thin coarse layer at 64.3', reddish-yellow, 10YR-5/6	64.4	0.4	64-66
Sand, medium-coarse, poorly-sorted, contains thin silty layer at 65.0', orange-yellow, 10YR-6/5	65.2	0.8	64-66
Sand, medium-coarse, reddish-orange, 5YR-5/5	65.4	0.2	64-66
Sand, fine with small quartz pebbles, poorly-sorted, some silt, light grayish-beige, 5Y-7/1	65.6	0.2	64-66
No Recovery	66.0	0.4	64-66
Sand, medium-coarse, poorly-sorted, orange-yellow, 2.5Y-6/6	66.2	0.2	66-68
Sand, medium-coarse, poorly-sorted, many small quartz pebbles, light gray, 5Y-7/1	66.6	0.4	66-68
Sand, medium-coarse, poorly-sorted, many small quartz pebbles, contains streaks of 2.5Y-7/5, yellowish-beige, 5Y-7/1	66.8	0.2	66-68
Sand, fine with some silt, contains some small quartz pebbles throughout and streaks of 2.5Y-7/4, light yellowish-beige, 2.5Y-7/1	67.2	0.4	66-68
Sand, fine, contains some small quartz pebbles, light yellowish-orange, 2.5Y-6/5	67.3	0.1	66-68
No Recovery	68.0	0.7	66-68
Sand, fine-medium, contains some small pebbles, light yellowish-orange, 2.5Y-6/5	68.3	0.3	68-70
Sand, medium-coarse, contains many small quartz pebbles, light yellowish-orange, 2.5Y-6/4	68.5	0.2	68-70
Sand, fine-medium, yellowish-beige, 10YR-6/5	68.6	0.1	68-70
Sand, coarse, contains many small quartz pebbles, yellowish-beige, 2.5Y-6/4	68.8	0.2	68-70
Sand, medium-coarse, contains a thin silty layer (5Y-8/1) at 68.95', yellowish-beige, 10YR-6/5	69.0	0.2	68-70
Sand, fine-medium, contains 2.5Y-6/4 swirls, yellowish-orange, 2.5Y-6/2	69.3	0.3	68-70
No Recovery	70.0	0.7	68-70
Sand, coarse, pebbly, orange-beige, 2.5Y-6/5	70.2	0.2	70-72
Sand, fine, contains small quartz pebbles, orange-beige, 10YR-6/6 with some 2.5Y-7/3	70.5	0.3	70-72
Sand, medium-coarse, beige, 2.5Y-6/2	70.6	0.1	70-72

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)	
Sand, medium-coarse, more well-sorted than prior interval, beige, 2.5Y-6/2	70.9	0.3	70-72	Generally medium-gray, fine silty sands with interlayered clays
Sand, fine, orange-beige, 10YR-6/5	71.1	0.2	70-72	
Sand, fine, gray, 2.5Y-5/1	71.3	0.2	70-72	
No Recovery	72.0	0.7	70-72	Kirkwood Formation
Sand, fine to silty, medium to dark gray, 2.5Y-4/1 (or gray chart 4/1)	73.0	1.0	72-74	
Silty sand, fine, medium to dark gray, contains 5-6 very dark gray laminations, 2.5Y-4/1 (or gray chart 4/1)	73.15	0.15	72-74	
Silty sand, fine, medium gray, 5/1 (gray chart)	73.5	0.35	72-74	
No Recovery	74.0	0.5	72-74	
Silty sand, fine, mottled last 0.4' of interval, gray, 5Y-4/1	75.5	1.5	74-76	
No Recovery	76.0	0.5	74-76	
Silty sand, fine, gray, 5Y-4/1	77.4	1.4	76-78	
No Recovery	78.0	0.6	76-78	
Silty sand, fine, contains thin dark layer of very fine silty sand at 78.45', gray, 5Y-4/1	79.7	1.7	78-80	
No Recovery	80.0	0.3	78-80	
Silty sand, fine, mottled throughout with dark, very fine silty clay, gray, 5Y-4/1	81.5	1.5	80-82	
No Recovery	82.0	0.5	80-82	
Silty sand, fine, contains a few dark gray, silty mottles at 82.8'-82.9', gray, 5Y-4/1	83.3	1.3	82-84	
No Recovery	84.0	0.7	82-84	
Silty sand, fine, contains darker silty bands at 84.9'-85.1', gray, 5Y-4/1	85.4	1.4	84-86	
No Recovery	86.0	0.6	84-86	
Silty sand, fine, contains dark silty mottles at 86.0' to 86.2' and 87.2' to 87.4', gray, 5Y-4/1	87.7	1.7	86-88	
No Recovery	88.0	0.3	86-88	
Silty sand, fine, contains dark gray silty sand (5Y-3/1) from 88.5'-88.9', gray, 5Y-4/1	89.5	1.5	88-90	
No Recovery	90.0	0.5	88-90	
Silty sand, fine, gray, 5Y-4/1	90.2	0.2	90-92	
Silty sand, fine, a little lighter gray, some mottles with darker silty sand, 5Y-5/1	90.9	0.7	90-92	
Silty sand, fine, a little darker gray, 5Y-3/1	91.2	0.3	90-92	
Silty sand, fine, gray, 5Y-4/1	91.5	0.3	90-92	
No Recovery	92.0	0.5	90-92	
Silty sand, fine, contains a few swirls of clay from 92.8' to 92.9', gray, 5Y-4/1	93.6	1.6	92-94	
No Recovery	94.0	0.4	92-94	
Silty sand, fine, gray, 5Y-4/1	94.4	0.4	94-96	
Silty sand, fine, contains swirls of dark gray clay, gray, 5Y-4/1	94.8	0.4	94-96	
Silty sand, fine, gray, 5Y-4/1	95.1	0.3	94-96	
Silty sand, fine, contains 1/2" band of dark gray clay with much mica, gray, 5Y-3/1	95.25	0.15	94-96	
Silty sand, fine, gray, 5Y-4/1	95.7	0.45	94-96	
No Recovery	96.0	0.3	94-96	
Silty sand, fine, contains thin bands/swirls of clay at 96.3' to 96.4' and 97.8' to 97.9', a little lighter gray, 5Y-5/1	97.4	1.4	96-98	
No Recovery	98.0	0.6	96-98	
Silty sand, fine, gray, 5Y-4/1	98.4	0.4	98-100	

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)	
Interlayered fine silty gray sand (5Y-4/1) and dark gray clay (5Y-2.5/1), some layers of clay are 1/2" to 3/4" thick	99.2	0.8	98-100	
No Recovery	100.0	0.8	98-100	
Interlayered fine silty sand (gray 5Y-4/1) and dark gray clay (5Y-2.5/1), some layers of clay are 1/2" to 3/4" thick	101.2	1.2	100-102	
Silty sand, fine, gray, 2.5Y-5/1	101.7	0.5	100-102	
No Recovery	102.0	0.3	100-102	
Silty sand, fine, gray, 2.5Y-5/1	102.5	0.5	102-104	
Interlayered fine silty sand (gray 5Y-4/1) and dark gray clay (5Y-2.5/1), some layers of clay are 1/2" to 3/4" thick	102.8	0.3	102-104	
Silty sand and clay, thinly laminated, gray, 5Y-4/1 and 5Y-2.5/1	103.4	0.6	102-104	
Silty sand, fine, gray, 2.5Y-5/1	103.6	0.2	102-104	
Clay, gray, 2.5Y-2.5/1	103.7	0.1	102-104	
No Recovery	104.0	0.3	102-104	
<i>End of continuous core. Drilled down to 110 ft to try and find confining unit.</i>	112.0	2.0	110-112	
Silty sand and mottled clay, gray, about 50/50, silty sand = 2.5Y-5/1, clay = 2.5Y-2.5/1	121.9	1.9	120-122	
<i>Drilled down to 120 ft to try and find confining unit.</i>	122.0	0.1	120-122	
Silty sand and mottled clay, gray, about 70/30, silty sand = 2.5Y-5/1, clay = 2.5Y-2.5/1	124.0	2.0	122-124	
Clay, tight, glauconitic, greenish-gray, 5GY-4/2				
Clay, tight, glauconitic, greenish-gray, 5GY-4/2				
<i>End of coring</i>				

SS2 Sediment Core; located near CM3 wells, approximately 45 ft south of CM3 and 65 ft north of CM9; 3/12/01; Dyer, Hayworth, Antworth

GPS Reading: N 40 02.264, W 74 25.874

Depth, refers to the bottom of the specified interval; alphanumeric codes at selected horizons refer to color designations as specified in the Munsell Soil Color Charts (1975), example (2.5Y-3/1)

Core barrels are 3.85' (0.15' is boot)--for total of 4.0 ft

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)
No Recovery	1.3	1.3	0-4
Peat, black, high organic matter, wetland sediments and fine roots, 1 large woody piece (1" x 0.5")	1.9	0.6	0-4
Sand, coarse, dark brown, 2.5YR-2.5/2, contains brick red coarse sand band, 2.5YR-3/5	2.0	0.1	0-4
Sand, medium-coarse, yellow/tan, 10YR-5/4	2.3	0.3	0-4
Sand, coarse, contains mm-sized quartz pebbles, beige 10YR-6/2	2.5	0.2	0-4
Sand and gravel, very coarse, contains quartz pebbles up to 3/4", mostly beige with some rust/orange, 10YR-6/2	2.8	0.3	0-4
Sand, coarse, gray, 10YR-6/1	3.0	0.2	0-4
Sand, coarse, grayish-beige, 10YR-7/1	3.4	0.4	0-4
Sand, coarse, grayish-beige, contains a few small black bands, 10YR-7/2	3.9	0.5	0-4
No Recovery (boot)	4.0	0.2	0-4
No Recovery	4.6	0.6	4-8
Sand, coarse, grayish-beige, 10YR-6/2	5.3	0.7	4-8
Sand, coarse, well-sorted, contains up to 3/4" quartz pebbles, grayish-beige, 10YR-7/2	5.8	0.5	4-8
Sand, coarse, less well-sorted than prior interval, contains up to 1/2" quartz pebbles, light orange-beige, 10YR-7/4	6.1	0.3	4-8
Sand, coarse, well-sorted, contains a few 1/2" quartz pebbles, beige-orange, 10YR-6/4	6.5	0.4	4-8
Sand, coarse, no pebbles, well-sorted, beige-orange, 10YR-6/4	6.8	0.3	4-8
Sand, medium-coarse, well-sorted, dark beige, 10YR-5/4	7.1	0.3	4-8
Sand, fine-medium, contains a few clayey blebs, orange-brown, 10YR-5/6	7.4	0.3	4-8
Sand, fine with some silt, dark orange-brown, 10YR-5/5	7.7	0.3	4-8
No Recovery (boot)	8.0	0.3	4-8
No Recovery	9.2	1.2	8-12
Sand, fine-medium, well-sorted, orange-brown, 10YR-5/5	10.0	0.8	8-12
Sand, fine-medium, well-sorted, contains black bands, orange-brown, 10YR-5/5	10.1	0.1	8-12
Sand, medium, well-sorted, one black band about half-way through interval, beige-orange, 10YR-6/4	10.9	0.8	8-12
Sand, medium-coarse, well-sorted, thin black bands at 11.1' and 11.4', beige, 10YR-6/2	11.8	0.9	8-12
No Recovery (boot)	12.0	0.2	8-12
No Recovery	13.3	1.3	12-16
Sand, medium, well-sorted, has many heavies throughout, beige, 2.5Y-6/2	14.1	0.8	12-16
Sand, medium, well-sorted, has many heavies throughout, contains 1 large black band, orange, 10YR-6/4	14.3	0.2	12-16
Sand, medium-coarse, has many heavies, coarsens downward toward end of interval, orange-beige, 10YR-6/5	15.0	0.7	12-16
Sand, medium to mostly coarse, has many heavies, continuing to coarsen downward, orange-beige, 10YR-6/5	15.5	0.5	12-16
Sand, very coarse, not many heavies, more orange, 10YR-5/6	15.8	0.3	12-16
No Recovery (boot)	16	0.2	12-16
No Recovery	16.6	0.6	16-20

Description	Depth (ft.)	Thickness (ft.)	Core Interval (ft.)
Sand, medium-coarse, orange-beige, 10YR-5/5	17.4	0.8	16-20
Sand, coarse, orange-brown, 7.5YR-5/5	17.5	0.1	16-20
Sand, medium-coarse, orange, 10YR-5/6	18.0	0.5	16-20
Sand, medium with some silt, dark orange (many heavies), 10YR-4/5	18.4	0.4	16-20
Sand, medium-coarse, beige with some heavies, 7.5YR-6/4	18.8	0.4	16-20
Sand, medium-coarse, contains several black bands, orange-beige, 7.5YR-5/6	19.4	0.6	16-20
Sand, fine-medium, contains some thin black bands, red, 2.5YR-4/5	19.8	0.4	16-20
No Recovery (boot)	20.0	0.2	16-20
No Recovery	21.4	1.4	20-24
Sand, fine-medium, well-sorted, reddish-orange, 2.5YR-5/6	22.0	0.6	20-24
Sand, medium-coarse (abrupt change from previous interval), not well-sorted, brownish-orange, 2.5YR-4/5	22.3	0.3	20-24
Silty sand with clay, (abrupt change from previous interval), brownish-orange, 2.5YR-4/5	22.4	0.1	20-24
Sand, coarse, brownish-orange, 2.5YR-4/5	23.8	1.4	20-24
No Recovery (boot)	24.0	0.2	20-24
No Recovery	25.2	1.2	24-28
Sand, coarse, brownish-orange, 2.5YR-4/5	25.4	0.2	24-28
Clay, contains pebbles (up to 1/4" diameter) and a range of sands, orange, 2.5YR-5/6	25.5	0.1	24-28
Sand, medium, contains occasional small blebs of clay and some pebbles, brownish-orange, 2.5YR-4/5	25.8	0.3	24-28
Sand, fine-medium, well-sorted, orange-brown, 2.5YR-3/5	26.2	0.4	24-28
Clay, orange-brown, 2.5YR-4/6	26.4	0.2	24-28
Fine sand/silty clay, orange-brown, 2.5YR-4/6	26.5	0.1	24-28
Fine sand/silty clay, orange-brown, 2.5YR-4/5	26.6	0.1	24-28
Sand, fine-medium, orange, gradually becoming lighter with depth, 2.5YR-5/5	27.2	0.6	24-28
Sand, fine-medium, orange, 2.5YR-6/5	27.8	0.6	24-28
No Recovery (boot)	28.0	0.2	24-28
No Recovery	29.6	1.6	28-32
Sand, fine-medium, well-sorted, brownish-orange, 5YR-6/5	29.9	0.3	28-32
Sand, fine-medium, well-sorted, brownish orange, 5YR-4/5	30.1	0.2	28-32
Sand, fine-medium, reddish-orange, 2.5YR-4/5	30.6	0.5	28-32
Sand, medium, contains a few dark, thin bands and occasional small pebbles, greenish-orange, 2.5YR-5/4	31.8	1.2	28-32
No Recovery (boot)	32.0	0.2	28-32
<i>End of Coring</i>			

SS3 Sediment Core; located approximately 25 ft SW of CM3 wells; 3/13/01; Dyer, Hayworth, Antworth  
 Coring aborted after 4 ft depth (drill-rig problems)

GPS Reading: none

Core barrels are 3.85' (0.15' is boot)--for total of 4.0 ft

Depth, refers to the bottom of the specified interval; alphanumeric codes at selected horizons refer to color designations as specified in the Munsell

Soil Color Charts (1975), example (2.5Y-3/1)

Description	Core		
	Depth (ft.)	Thickness (ft.)	Interval (ft.)
No Recovery	2.2	2.2	0-4
Surface roots and twigs	2.25	0.05	0-4
Black silt, roots and twigs	2.7	0.45	0-4
Sand, coarse, contains many large quartz pebbles (up to 1" diameter), grades from dark gray to light gray with depth, 2.5YR-5/1 to 2.5YR-7/1	3.8	1.1	0-4
No Recovery (boot)	4.0	0.2	0-4
<i>End of coring</i>			